

TITLEPOLYMERIZATION WITH LIVING CHARACTERISTICS

Ans 41

BACKGROUND OF THE INVENTION

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This invention relates to a free radical polymerization process with characteristics of a living polymerization system in that it is capable of producing polymers of pre-determined molecular weight with narrow molecular weight distribution (low polydispersity), and, by successively adding different monomers. can be used to make block polymers. The process can be used to produce polymers of more complex architecture, including variously branched homo- and copolymers. The use of certain reagents in this process and the polymers produced thereby are also claimed. Novel chain transfer agents for use in the process are also claimed.

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There is increasing interest in methods for producing a variety of polymers with control of the major variables affecting polymer properties. Living polymerizations provide the maximum degree of control for the synthesis of polymers with predictable well defined structures. The characteristics of a living polymerization are discussed by Quirk and Lee (*Polymer International* 27, 359 (1992)) who give the following experimentally observable criteria:

20

- "1. Polymerization proceeds until all of the monomer has been consumed. Further addition of monomer results in continued polymerization.
2. The number average molecular weight (or the number average degree of polymerization) is a linear function of conversion.
3. The number of polymer molecules (and active centers) is a constant which is sensibly independent of conversion.
4. The molecular weight can be controlled by the stoichiometry of the reaction.
5. Narrow molecular weight distribution polymers are produced.
6. Block copolymers can be prepared by sequential monomer addition.
7. Chain end-functionalized polymers can be prepared in quantitative yield. "

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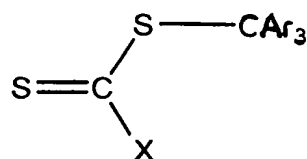
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Living polymerization processes can be used to produce polymers of narrow molecular weight distribution containing one or more monomer sequences whose length and composition are controlled by the stoichiometry of the reaction

and the degree of conversion. Homopolymers, random copolymers or block polymers can be produced with a high degree of control and with low polydispersity. Swarc (*Adv. Polym. Sci.* **49**, 1 (1983)) stated that living polymerization to give polymers of narrow molecular weight distribution requires the absence of chain transfer and termination reactions, the elementary reactions being only initiation and propagation, which take place uniformly with respect to all growing polymer chains. Later Inoue and Aida in an article on living polymer systems (*Encyclopedia of Polymer Science and Engineering*, Supplement Volume, Wiley Interscience New York 1989) stated "If chain transfer and terminating agents are present in the polymerization system the living character of the polymerization is lost, and the formation of polymer with narrow molecular weight distribution does not result."

However, it has been shown that if the chain transfer process is reversible then polymerization can still possess most of the characteristics of living polymerization. A variety of terms have been used to describe polymerizations believed to involve this mechanism including "immortal polymerization", "equilibration polymerization", "polymerization with degenerative chain transfer" and "living polymerization with reversible chain transfer". Quirk and Lee (*Polymer International* **27**, 359 (1992)), who recommend the last terminology, point out that the Criteria 3 and 4 mentioned above need to be modified when describing these polymerizations to encompass the fact that the total number of polymer molecules is determined by the total number of moles of transfer agent plus the number of moles of initiator.

Block copolymer syntheses by free radical polymerization in the presence of certain dithiocarbamate or xanthate derivatives as initiator-transfer agents-chain terminators (iniferters) have been described. In these examples the dithiocarbamate or xanthate derivative is used as a photochemical initiator. For a discussion of this chemistry see recent reviews [Moad *et al.* in *Comprehensive Polymer Science*; Pergamon: London, vol 3, p 141 (1989)]. The dithiocarbamates (for example, benzyl dithiocarbamate) have very low transfer constants ($\ll 0.1$) and are ineffective in the context of the current invention. Greszta *et al.* (*Macromolecules*, **27**, 638 (1994)) have described the application of chain transfer chemistry in living radical polymerization and have proposed and rejected the use of dithiocarbamates in this context because of the low transfer constant and the problem of side reactions. JP 04198303 A2 discloses polymerization in the presence of triarylmethyl dithiocarboxylates of the following structure

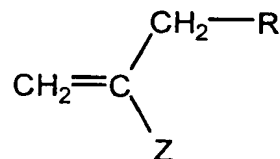


X=alkyl or aryl

as initiators of polymerization to yield block polymers which may have low polydispersity (all examples have $M_w/M_n \approx 1.4$). These compounds have a very weak carbon-sulfur bond that cleaves under polymerization conditions to give a stable triarylmethyl radical and a thiocarbonylthiyl radical. The product triarylmethyl radical is known to be a poor initiator of radical polymerization. They are thus ineffective in the context of this invention.

Rizzardo *et al.* (*Macromol. Symp.* **98**, 101 (1995)) review polymerization in the presence of addition-fragmentation chain transfer agents but do not mention the possibility of low polydispersity products.

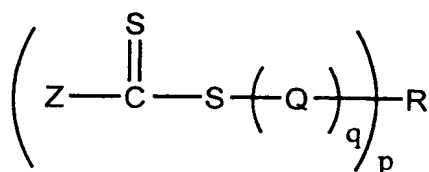
Polymers or oligomers of the following structure are known as macromonomers.



These macromonomers which are addition-fragmentation chain transfer agents are disclosed in *J Macromol. Sci.- Chem.* **A23**, 839 (1986) and International Patent publications WO 93/22351 and WO 93/22355. Free radical polymerization with living characteristics utilizing these macromonomers as chain transfer agents is disclosed in International Patent Application PCT/US95/14428. The process of this invention has the advantages of compatibility with a wide range of monomers and reaction conditions and will give good control over molecular weight, molecular weight distribution, i.e., polydispersity, and polymer architecture.

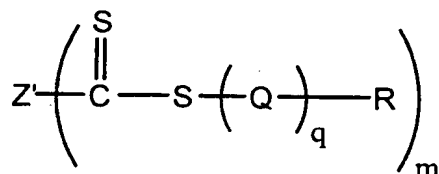
SUMMARY OF THE INVENTION

This invention concerns a process for the synthesis of polymers of the general Formula:



Formula A

and

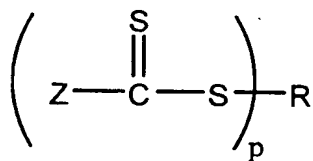


Formula B

comprising contacting:

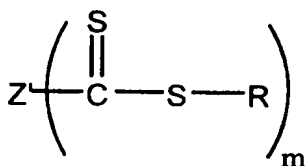
- (i) a monomer (means one or more) selected from the group consisting of vinyl monomers (of structure $\text{CH}_2=\text{CUV}$), maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

- (ii) a thiocarbonylthio compound selected from:



Formula C

and



Formula D

having a chain transfer constant greater than about 0.1; and

- (iii) free radicals produced from a free radical source; and

controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii);

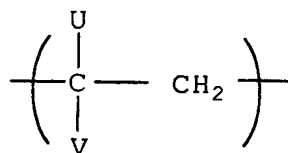
the polymer of Formula A being made by contacting (i), (ii)C and (iii) and the
5 polymer of Formula B being made by contacting (i), (ii) D and (iii);

wherein:

10 Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxy carbonyl, optionally substituted aryloxy carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O₂CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl-phosphinato
15 [-P(=O)R"2], and a polymer chain formed by any mechanism;

Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of
20 aliphatic carbon, aromatic carbon, and sulfur;

Q is selected from the group consisting of



and

25 repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

U is selected from the group consisting of hydrogen, halogen, optionally substituted C₁-C₄ alkyl wherein the substituents are independently selected from the group that consists of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, aryloxy (O₂CR"), alkoxy- carbonyl and aryloxy-carbonyl (CO₂R");
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V is selected from the group consisting of hydrogen, R", CO₂H, CO₂R", COR", CN, CONH₂, CONHR", CONR"2, O₂CR", OR" and halogen;

5 R is selected from the group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic species; and a polymer chain prepared by any polymerization mechanism; in compounds C and D, R• is a free-radical leaving group that initiates free radical polymerization;

10 R" is selected from the group consisting of optionally substituted C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

15 q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when $p \geq 2$, then $R=R'$;

m is an integer ≥ 2 ; and

20 R' is a p-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; in compounds C and D, R• is a free radical leaving group that initiates free radical polymerization.

25 Preferred is a process as described for controlling polydispersity by varying the ratio of the number of molecules of (ii) to (iii) as follows:

- 30 (a) lower polydispersity by increasing the ratio of (ii) to (iii); and
(b) increase polydispersity by decreasing the ratio of (ii) to (iii).

Most preferred is the process in which the ratio of (ii) to (iii) is increased to obtain a polymer having a polydispersity below about 1.5.

35 The monomer moieties and value of q in the monomer repeating unit(s) derived from those in (i) are selected so that:
when $q \geq 1$ and Q is a single monomer species, then the polymer is homopolymer;

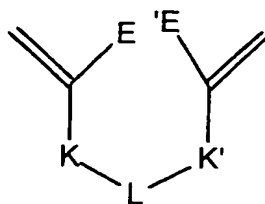
when $q \geq 2$ and Q is selected from 2 or more different monomer species in irregular sequence then the polymer is copolymer; and
 when $q \geq 2$ and Q is selected from 2 or more different monomer species in which each different monomer or group of monomers appears in a discrete sequence then the polymer is block copolymer.

The invention also concerns chain transfer agents designated hereafter as (5), (6), (7), (8), (9), (10), (11), (14), (15), (17), (18), (19), (22), (23), (24), (25), (28) and (29). The invention also concerns polymers of Formulae A and B with substituents as defined above. In polymers of Formulae A and B, R^\bullet and R'^\bullet are derived from free radical leaving group(s) that initiate free radical polymerization, $R-(Q)_q^\bullet$ and $R'-(Q)_q^\bullet$ being the free radical leaving group(s) that initiate free radical polymerization. Preferred polymers are random, block (most preferred), graft, star and gradient copolymers; most especially those having chain-end functionality. Compounds of Formulae C and D can be used to produce branched, homo- or copolymers with the number of arms being less than or equal to p in C and m in D.

Definitions

By polymer chains formed by any mechanism (in Z or R), is meant: condensation polymers such as polyesters (for example, polycaprolactone, polyethylene terephthalate), polycarbonates, poly(alkylene oxide)s [for example, poly(ethylene oxide), poly(tetramethylene oxide)], nylons, polyurethanes and chain polymers such as poly(meth)acrylates and polystyrenics.

Cyclopolymerizable monomers are compounds which contain two or more unsaturated linkages suitably disposed to allow propagation by a sequence of intramolecular and intermolecular addition steps leading to the incorporation of cyclic units into the polymer backbone. Most compounds of this class are 1,6-dienes such as - diallylammonium salts (e.g., diallyldimethylammonium chloride), substituted 1,6-heptadienes (e.g., 6-dicyano-1,6-heptadiene, 2,4,4,6-tetrakis(ethoxycarbonyl)-1,6-heptadiene) and monomers of the following generic structure



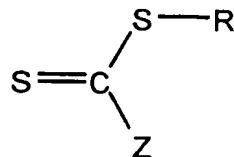
where substituents K, K', L, E, E' are chosen such that the monomer undergoes cyclopolymerization. For example:

- 5 *Sub A2* E, E' are independently selected from the group consisting of H, CH₃, CN, CO₂Alkyl, Ph; K, K' are selected from the group consisting of CH₂, C=O, Si(CH₃)₂, O; L is selected from the group consisting of C(E)₂, O, N(Alkyl)₂ salts, P(Alkyl)₂ salts, P(O)Alkyl. For a further list of monomers see Moad and
- 10 Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995, pp 162-170.

- By organometallic species is meant a moiety containing one or more metal atoms from Groups III and IV of the Periodic Table and transition elements and organic ligands, preferably species such as Si(X)₃, Ge(X)₃ and Sn(X)₃ which can
- 15 be good radical leaving groups and initiate polymerization.

DETAILS OF THE INVENTION

- We have now discovered that free radical polymerizations when carried
- 20 out in the presence of certain chain transfer agents of the following structure:

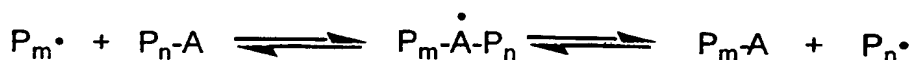
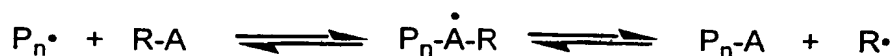
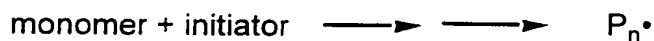


have living characteristics and provide polymers of controlled molecular weight and low polydispersity. Chain transfer agents applicable in this invention are designated as CTAs hereinafter.

- 25 While not wishing to be limited to any particular mechanism, it is believed that the mechanism of the process is as summarized in Scheme 1 below. Propagating radicals P_n• are produced by radical polymerization. These can react reversibly with the chain transfer agent RA to form an intermediate radical P_nA(•)R which fragments to give a radical R• (which adds monomer to reinitiate
- 30 polymerization) and a new transfer agent P_nA. This new transfer agent P_nA has similar characteristics to the original transfer agent RA in that it reacts with

another propagating radical P_m^\bullet to form an intermediate radical $P_nA(\bullet)P_m$ which fragments to regenerate P_n^\bullet and form a new transfer agent P_mA which has similar characteristics to RA. This process provides a mechanism for chain equilibration and accounts for the polymerization having living characteristics.

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Scheme 1:

P_n^\bullet and P_m^\bullet are propagating radicals of chain length n and m respectively.

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R^\bullet is a chain transfer agent derived radical which can initiate polymerization to produce a new propagating radical.

RA, P_nA and P_mA are CTAs.

This invention provides a free radical polymerization process with living characteristics which process comprises polymerizing one or more free radically polymerizable monomers in the presence of a source of initiating free radicals and a chain transfer agent (CTA) of Formula C or D which CTA during the polymerization reacts with the initiating or propagating radicals to give both a new radical that initiates further polymerization and a polymeric CTA also of Formula C or D (where R is the former initiating or propagating radical) with similar characteristics to the original CTA, the reaction conditions being chosen so that the ratio of the total number of initiator-derived radicals to the number of CTA molecules is maintained at a minimum value consistent with achieving an acceptable rate of polymerization, preferably less than 0.1, and the chain transfer constants of the CTAs are greater than 0.1, preferably greater than 1, and more preferably, greater than 10.

Initiating radicals are free radicals that are derived from the initiator or other species which add monomer to produce propagating radicals. Propagating radicals are radical species that have added one or more monomer units and are capable of adding further monomer units.

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All of the benefits which derive from the use of radical polymerization can now be realized in syntheses of low polydispersity homo- and copolymers. The ability to synthesize block, graft, star, gradient and end-functional polymers

further extends the value of the process as does compatibility with protic monomers and solvents.

The source of initiating radicals can be any suitable method of generating free radicals such as the thermally induced homolytic scission of a suitable compound(s) (thermal initiators such as peroxides, peroxyesters, or azo compounds), the spontaneous generation from monomer (*e.g.*, styrene), redox initiating systems, photochemical initiating systems or high energy radiation such as electron beam, X- or gamma-radiation. The initiating system is chosen such that under the reaction conditions there is no substantial adverse interaction of the initiator or the initiating radicals with the transfer agent under the conditions of the experiment. The initiator should also have the requisite solubility in the reaction medium or monomer mixture.

Thermal initiators are chosen to have an appropriate half life at the temperature of polymerization. These initiators can include one or more of the following compounds:

2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyano-2-butane), dimethyl 2,2'-azobisdimethylisobutyrate, 4,4'-azobis(4-cyanopentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]-propionamide, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramine), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl) ethyl] propionamide), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl) propionamide], 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis(2,2,4-trimethylpentane), 2,2'-azobis(2-methylpropane), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxy pivalate, t-butyl peroxy pivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl hyponitrite, dicumyl hyponitrite.

Photochemical initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate quantum yield for radical production under the conditions of the polymerization. Examples

include benzoin derivatives, benzophenone, acyl phosphine oxides, and photo-redox systems.

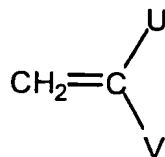
Redox initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate rate of radical production under the conditions of the polymerization; these initiating systems can include combinations of the following oxidants and reductants:

oxidants: potassium peroxydisulfate, hydrogen peroxide, t-butyl hydroperoxide.

reductants: iron (II), titanium (III), potassium thiosulfite, potassium bisulfite.

Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995, pp 53-95.

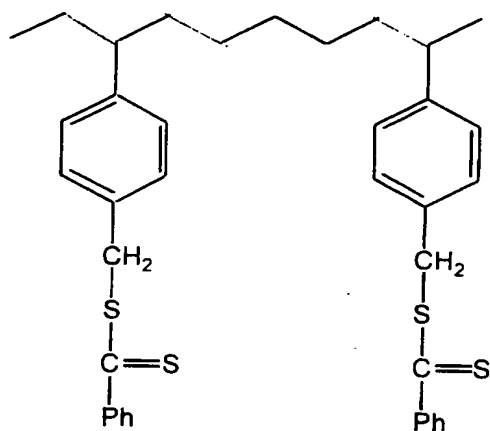
The process of the invention can be applied to any monomers or monomer combinations which are susceptible to free-radical polymerization. Such monomers include those with the general structure:



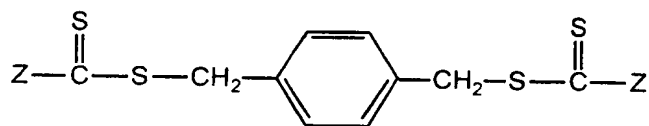
where U and V are as defined above. Optionally, the monomers are selected from the group that consists of maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers. Monomers $\text{CH}_2=\text{CUV}$ as used herein include acrylate and methacrylate esters, acrylic and methacrylic acid, styrene, acrylamide, methacrylamide, and methacrylonitrile, mixtures of these monomers, and mixtures of these monomers with other monomers. As one skilled in the art would recognize, the choice of comonomers is determined by their steric and electronic properties. The factors which determine copolymerizability of various monomers are well documented in the art. For example, see: Greenley, R.Z., in Polymer Handbook 3rd Edition (Brandup, J., and Immergut, E.H Eds.) Wiley: New York, 1989 p II/53.

Specific monomers or comonomers include the following: methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate,

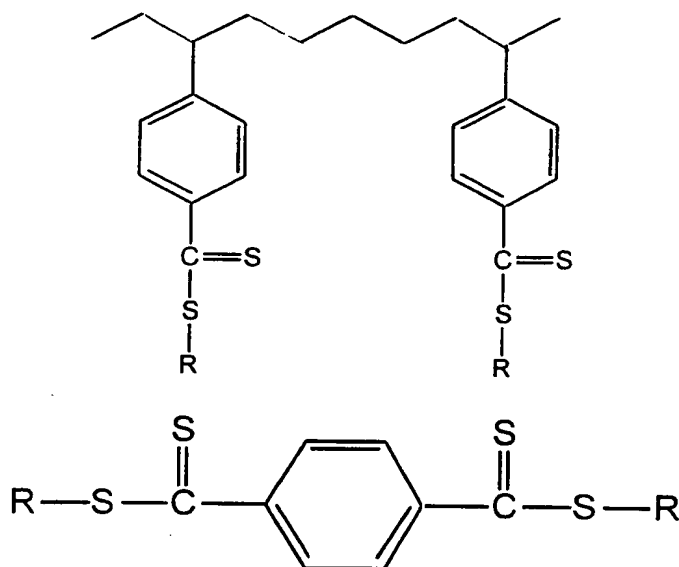
- methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene. methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates,
- 5 acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate,
- 10 hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-tert-butylmethacrylamide, N-n-butylmethacrylamide, N-methylolmethacrylamide, N-ethylolmethacrylamide, N-tert-butylacrylamide, N-n-butylacrylamide, N-
- 15 methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), diethylaminostyrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers). p-vinylbenzene sulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate,
- 20 dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropylmethacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate,
- 25 triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl
- 30 benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene, chloroprene, ethylene, propylene.

Examples of multifunctional ($p \geq 2$) structures represented by Formula C

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Examples of multifunctional ($m \geq 2$) structures represented by Formula D



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Many such structures are possible of which the following compounds are illustrative. Additional structures are found in the Examples section.

In the compounds of Formulae C and D substituted rings can have reactive substituent groups directly or indirectly attached to the ring by means of a methylene group or other side chain.

The substituents on groups referred to above for R, R', R'', Z, Z' in Formulae A-D and U, V, R'' in the monomer do not take part in the polymerization reactions but form part of the terminal groups of the polymer chains and may be capable of subsequent chemical reaction. The low polydispersity polymer containing any such reactive group is thereby able to undergo further chemical transformation, such as being joined with another polymer chain. Suitable reactive substituents include: epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkylcarbonyloxy, isocyanato, cyano, silyl, halo, and dialkylamino. Alternatively, the substituents may be non-reactive such as alkoxy, alkyl or aryl. Reactive groups should be chosen such that there is no adverse reaction with the CTA under the conditions of the experiment. For example, groups such as primary or secondary amino ($-NH_2$, $-NHalkyl$) under some conditions may react with dithioesters to give thioamides thus destroying the CTA.

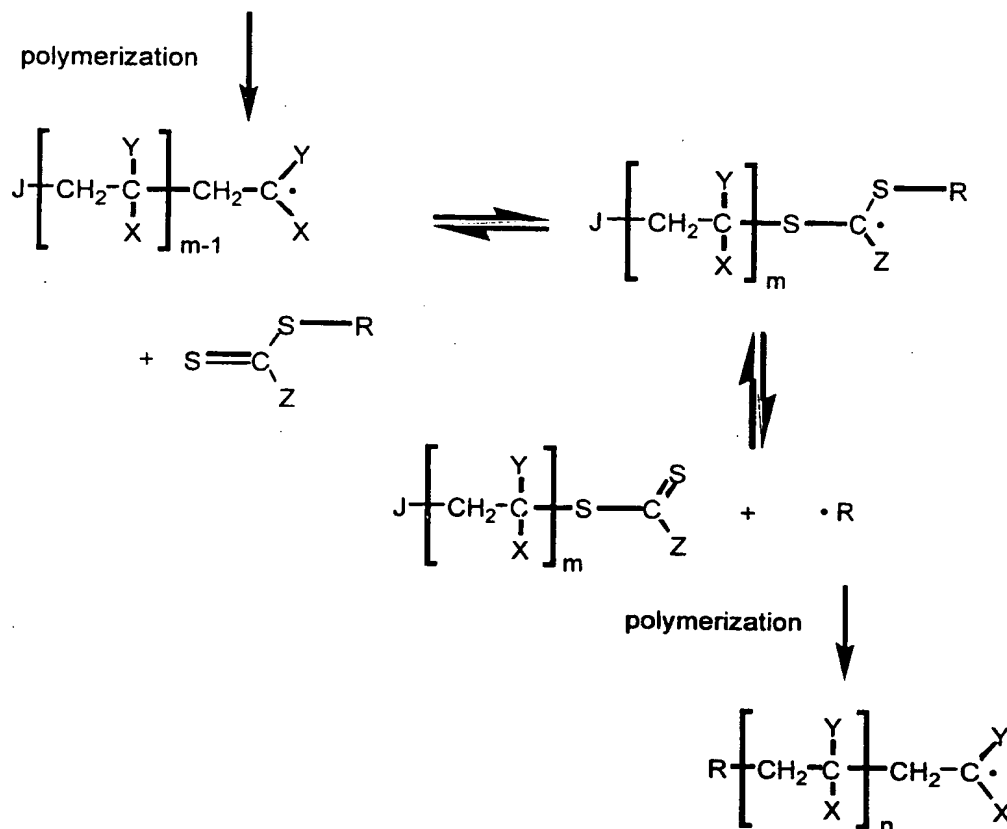
Unless specified otherwise alkyl groups referred to in this specification may be branched or unbranched and contain from 1 to 18 carbon atoms. Alkenyl groups may be branched or unbranched and contain from 2 to 18 carbon atoms.

Saturated, unsaturated, or aromatic carbocyclic or heterocyclic rings may contain from 3 to 14 atoms.

"Heterocyclic" or "heterocyclyl" means a ring structure containing 3 to 10 atoms at least one of which is selected from O, N and S, which may or may not be aromatic. Examples of aromatic "heterocyclyl" moieties are pyridyl, furanyl, thienyl, piperidiny, pyrrolidiny, pyrazoyl, benzthiazoyl, indolyl, benzofuranyl, benzothiophenyl, pyrazinyl, quinolyl, and the like, optionally substituted with one or more alkyl, haloalkyl, halo, nitro, or cyano groups. "Ph" means phenyl.

An example of the preferred class of CTAs are the dithioesters (Formula C, p=1) such as are depicted in Scheme 2 which is illustrative of the reaction mechanism believed to be operative in the process of this invention. It should be understood, however, that the invention is not limited to the mechanism depicted and that other mechanisms may be involved.

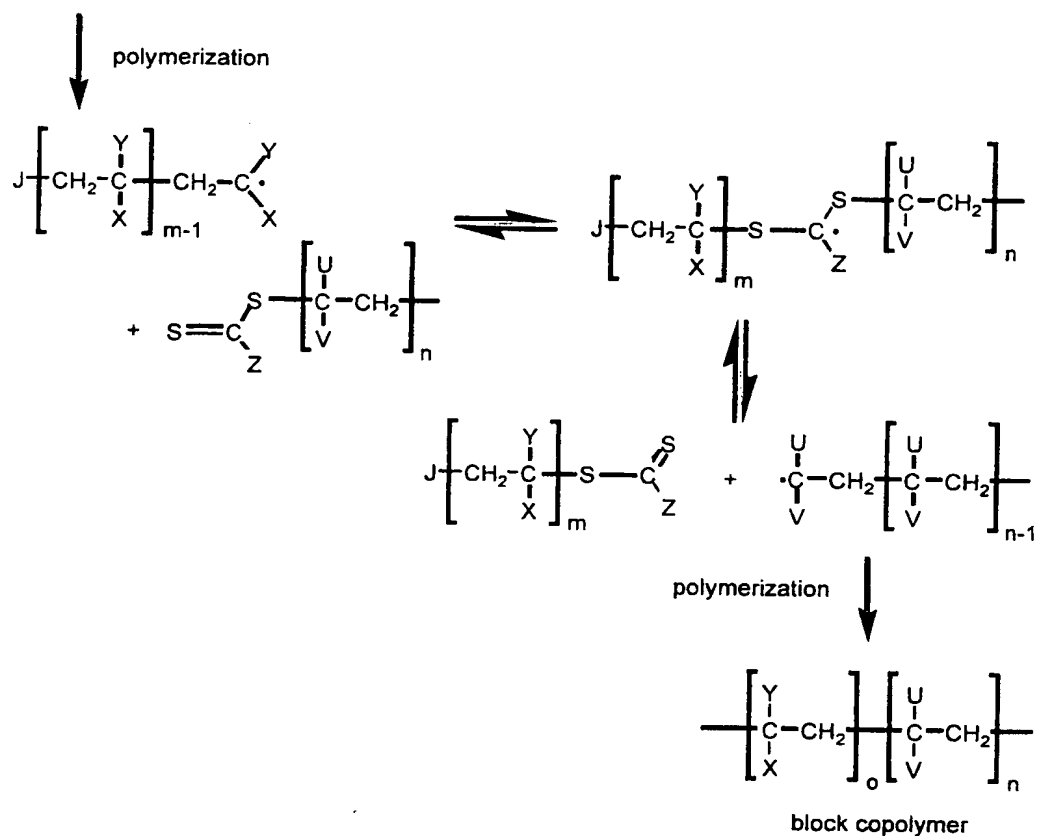
Scheme 2:



J is a fragment derived from an initiating or propagating radical.

A key feature of the invention is the retention of the active thiocarbonylthio end group $[-C(S)-S-]$ in the polymeric product. The invention thus also provides a route to block polymers as illustrated, for example, in Scheme 3.

Scheme 3:

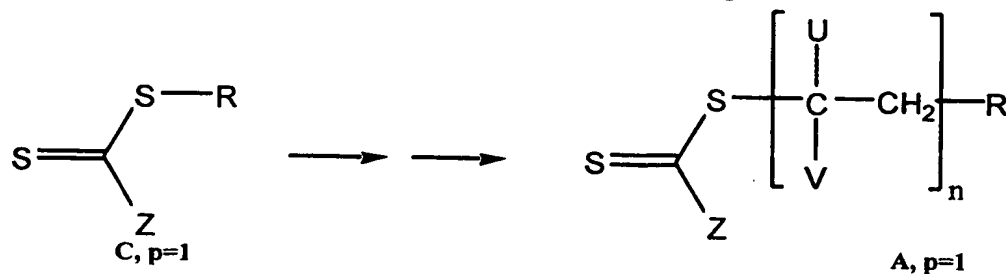


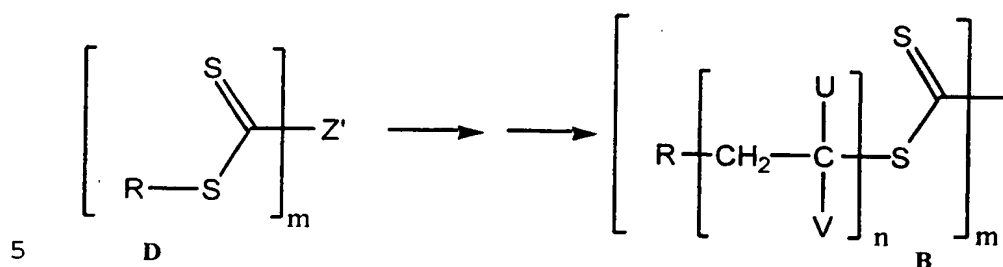
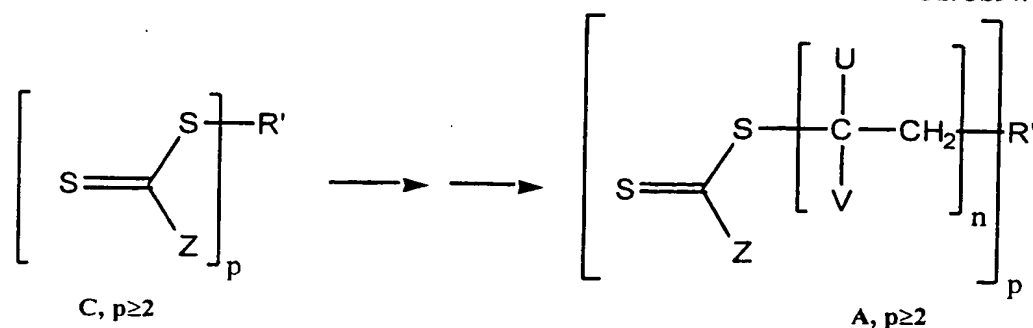
J is a fragment derived from an initiating or a propagating radical.

Polymers with complex architectures including multiblock, branched, star and graft polymers are available through the use of reagents containing multiple thiocarbonylthio groups as indicated by formulae C (where $p \geq 2$) and D. The overall process is shown in Scheme 4.

Scheme 4:

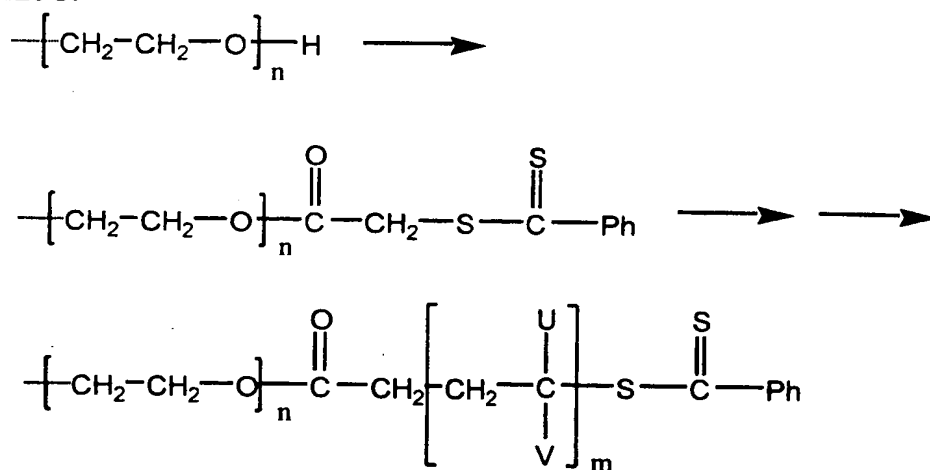
Formation of linear polymer from CTA of formula C, $p=1$





Block, star or graft polymers can be formed from polymers (prepared by any polymerization mechanism) that contain the thiocarbonylthio [-S-C(=S)-] linkage. Methods for forming dithoester and related groups are well-documented in the art. The following example (Scheme 5) of forming a block copolymer from poly(ethylene oxide) is illustrative of the process.

Scheme 5:



Benefits of the polymerization process described in this invention are:

- a) Low polydispersity polymers can be synthesized.

In the context of the present invention, low polydispersity polymers are those with polydispersities that are significantly less than those produced by conventional free radical polymerization. In conventional free radical polymerization, polydispersities (the polydispersity is defined as the ratio of the weight average and number average molecular weights - M_w/M_n) of the polymers formed are typically in the range 1.6-2.0 for low conversions (<10%) and are substantially greater than this for higher conversions. Polydispersities obtained with the present invention are usually less than 1.5, often less than 1.3 and, with appropriate choice of the chain transfer agent and the reaction conditions, may be less than 1.1. The low polydispersity can be maintained at high conversions (see Examples).

Note that it is also possible to produce polymers with broad, yet controlled, polydispersity or multimodal molecular weight distribution by controlled addition of the CTA over the course of the polymerization process.

Müller et al. have derived relationships which enable polydispersities to be estimated for polymerizations which involve chain equilibration by reversible chain transfer (Müller, A.H.E.; Zhuang, R.; Yan, D.; Litvenko, G. *Macromolecules*, **1995**, 28, 4326)

$$M_w/M_n = 1 + 1/C_{tr}$$

This above relationship should apply to batch polymerizations carried to full conversion in the situation where the number of initiator-radical derived chains is small with respect to total chains and there are no side reactions.

This relationship suggests that the transfer constant should be > 2 to obtain a polydispersity < 1.5 in a batch polymerization. If the transfer constant is < 2 , low polydispersities (< 1.5) may still be obtained in feed polymerization processes by choosing an appropriate monomer to transfer agent ratio and continuing the polymerization for a sufficient period to produce the desired molecular weight and polydispersity. In these circumstances, kinetic simulation can be used to aid in selecting reaction conditions.

In theory, it is possible to use reagents with very low transfer constants (< 0.1). However, in this case it is likely that side reactions will complicate the polymerization process. In practice, polydispersities are

- $$10 \quad MW_{\text{prod}} = \frac{[\text{moles monomer consumed}]}{[\text{moles CTA}]} \times MW_{\text{mon}} + MW_{\text{cta}}$$

MW_{mon} is the molecular weight of the monomer

15

Note that this form of molecular weight control is very different to that seen in free radical polymerization in the presence of conventional transfer agents.

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- i) The much higher transfer constant of compounds of Formula C or D (transfer constant can be >20) in comparison to macromonomers (transfer constant <2) means that it is not necessary to use starved-feed conditions to obtain low polydispersity polymers or block polymers. It is possible to use a batch polymerization process (see Examples).

Case	Age	Sex	Occupation	Onset	Duration	Course	Outcome
1	25	M	Student	1980	10 years	Chronic	Recovery
2	30	F	Teacher	1982	5 years	Chronic	Recovery
3	35	M	Engineer	1985	3 years	Chronic	Recovery
4	40	F	Homemaker	1988	2 years	Chronic	Recovery
5	45	M	Manager	1990	1 year	Chronic	Recovery
6	50	F	Retired	1992	6 months	Chronic	Recovery
7	55	M	Farmer	1995	4 months	Chronic	Recovery
8	60	F	Teacher	1998	3 months	Chronic	Recovery
9	65	M	Engineer	2000	2 months	Chronic	Recovery
10	70	F	Homemaker	2002	1 month	Chronic	Recovery

- ii) The compounds of Formula C or D do not undergo copolymerization with monomers. Therefore, low polydispersity polymers based on monosubstituted monomers (e.g., acrylic monomers, styrene) can be carried out under a wider range of reaction conditions.

5

The choice of the CTA compound is important in synthesis of low polydispersity polymers. The preferred dithioesters and related compounds give chain transfer with high chain transfer constants.

The transfer constant is defined as the ratio of the rate constant for chain transfer to the rate constant for propagation at zero conversion of monomer and CTA compound. If chain transfer occurs by addition-fragmentation, the rate constant for chain transfer (k_{tr}) is defined as follows:

$$k_{tr} = k_{add} \times \frac{k_{\beta}}{k_{-add} + k_{\beta}}$$

where k_{add} is the rate constant for addition to the CTA and k_{-add} and k_{β} are the rate constants for fragmentation in the reverse and forward directions respectively. Based on the addition-fragmentation mechanism, four factors can be seen to influence the effectiveness of the CTA in the process of this invention:

- a) The rate of reaction of the CTA (RA and AP_n in Scheme 1).
- b) The partitioning of the intermediate radicals (P_nA^*R and $P_nA^*P_m$ in Scheme 1) between starting materials and products.
- c) The rate of fragmentation of the intermediate radicals (P_nA^*R and $P_nA^*P_m$ in Scheme 1).
- d) The ability of the expelled radicals (R^* and P_n^* in Scheme 1) to reinitiate polymerization. Factors a) and b) determine the magnitude of the transfer constant of the CTA compound.

Preferably, the transfer constant for the addition-fragmentation chain transfer process is >0.1 . The polydispersity obtained under a given set of reaction conditions is sensitive to the value of the transfer constant. Lower polydispersities will result from the use of reagents with higher transfer constants. Benzyl dithiobenzoate derivatives have transfer constants which are estimated to be >20 in polymerization of styrene or acrylate esters. Higher transfer constants also allow greater flexibility in the choice of reaction conditions. For reagents with low chain transfer constants, the use of feed addition is advantageous to obtain low polydispersities.

The chain transfer activity of CTAs of Formula C or D is a function of the substituents R and Z and the particular propagating radical. R should be chosen

so as to be a free radical leaving group under the polymerization conditions (and yet retain ability to reinitiate polymerization - see below). In styrene polymerization, dithiobenzoate CTAs (RA in Scheme 1) where A is PhCS_2 - and R is $-\text{C}(\text{Me})_2\text{Ph}$, $-\text{C}(\text{Me})_2\text{CN}$, $-\text{C}(\text{Me})_2\text{CO}_2\text{Alkyl}$, $-\text{C}(\text{Me})_2\text{CH}_2\text{C}(\text{Me})_3$, $-\text{C}(\text{Me})_3$, $-\text{C}(\text{Me})\text{HPh}$, $-\text{CH}_2\text{Ph}$, $-\text{CH}_2\text{CO}_2\text{H}$ are all effective in giving narrowed polydispersity and molecular weight control under batch polymerization conditions (see Examples). On the other hand, in MMA polymerization, effectiveness decreases in the order where R is: $-\text{C}(\text{Me})_2\text{Ph}^3 > -\text{C}(\text{Me})_2\text{CN} > -\text{C}(\text{Me})_2\text{CO}_2\text{Alkyl} > -\text{C}(\text{Me})_2\text{CH}_2\text{C}(\text{Me})_3, -\text{C}(\text{Me})_3 > -\text{C}(\text{Me})\text{HPh} > -\text{CH}_2\text{Ph}$. Of these reagents, only those dithiobenzoates where R = $-\text{C}(\text{Me})_2\text{Ph}$ or $-\text{C}(\text{Me})_2\text{CN}$ are effective in giving both narrowed polydispersity and molecular weight control under batch polymerization conditions. The dithiobenzoate where R = $-\text{C}(\text{Me})_2\text{CO}_2\text{Et}$ provides good molecular weight control but broader polydispersity. These results can be related to the magnitude of the transfer constant for the CTA and to the free radical leaving group ability of the R substituent with respect to that of the propagating radical. For example, the dithiobenzoates with R = $-\text{C}(\text{Me})\text{HPh}$ and $-\text{CH}_2\text{Ph}$, which are ineffective in providing living characteristics to the batch polymerization of MMA at 60°C , have transfer constants of 0.15 and 0.03 respectively. These R groups are poor free radical leaving groups with respect to the MMA propagating radical.

It is also important to bear these considerations in mind in block copolymer synthesis. For example, the polystyryl propagating species ($-\text{P}_n = -[\text{CH}_2\text{-CHPh}]_n$ in Scheme 1) is a poorer free radical leaving group than the poly(methyl methacrylate) propagating species ($-\text{P}_n = -[\text{CH}_2\text{-C}(\text{Me})(\text{CO}_2\text{Me})]_n$ in Scheme 1). Thus, for synthesis of poly(methyl methacrylate-*block*-styrene) under batch polymerization conditions the poly(methyl methacrylate) block is made first in order to make a narrow polydispersity block copolymer.

If the reaction is carried out under conditions whereby the monomer is fed to maintain a lower monomer to CTA ratio, reagents with lower transfer constants can be used successfully. Thus, a polystyrene polymeric CTA has been successfully converted to poly(methyl methacrylate-*block*-styrene) under feed polymerization conditions.

Z in formulae C and D should be chosen to give a high reactivity of the double bond towards addition (while not slowing the rate of fragmentation to the extent that there is an unacceptable retardation of polymerization - see below). For example, the transfer constant increases in the series where $\text{Z} = -\text{NMe}_2 < -\text{OMe} < -\text{SMe} < -\text{Me} < -\text{Ph}$. The compound $\text{Z} = \text{NEt}_2$, $\text{R} = \text{CH}_2\text{Ph}$ has a very low transfer constant (<0.01) and is ineffective in polymerizations of styrene and

methyl methacrylate and vinyl acetate. Xanthate esters ($Z = -O\text{-alkyl}$) also have low transfer constants in polymerizations of styrene and methyl methacrylate (0.1) and are not effective in imparting living characteristics to polymerizations of these monomers. These compounds are not part of the present invention.

5 On the other hand, dithiocompounds with $Z = -S\text{-alkyl}$, $-alkyl$ or $-aryl$ (and other substituents as defined herein) have high transfer constants (the compound $Z = Ph$, $R = CH_2Ph$ has a transfer constant of >20 in styrene polymerization at $60^\circ C$) and are effective.

Factors c) and d), as set out above, determine whether or not there is
10 retardation of polymerization and the extent of any retardation. If the overall rate of reinitiation is greater than or equal to the rate of propagation there will be no retardation. These factors will be influenced by the substituents R and Z in formulae C and D and the nature of the propagating radical.

We have also found that the relative rates of addition and of fragmentation
15 can be estimated using molecular orbital calculations (For details of the method see Moad, G., Moad, C.L., Rizzardo, E., and Thang, S.H., *Macromolecules*, 1996, 29, 7717). This method and information on radical reactivities (see for example Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995), when taken together with the information provided herein, will
20 assist those skilled in the art in selecting transfer agents for particular polymerizations.

For heterogeneous polymerization, it is desirable to choose a CTA which has appropriate solubility parameters. For aqueous emulsion polymerization, the CTA should preferably partition in favour of the organic (monomer) phase and yet
25 have sufficient aqueous solubility that it is able to distribute between the monomer droplet phase and the polymerization locus.

The choice of polymerization conditions is also important. The reaction temperature will influence the rate parameters discussed above. For example, higher reaction temperatures will typically increase the rate of fragmentation.
30 Conditions should be chosen such that the number of chains formed from initiator-derived radicals is minimized to an extent consistent with obtaining an acceptable rate of polymerization. Termination of polymerization by radical-radical reaction will lead to chains which contain no active group and therefore cannot be reactivated. The rate of radical-radical termination is proportional to the
35 square of the radical concentration. Furthermore, in the synthesis of block star or branched polymers, chains formed from initiator-derived radicals will constitute a linear homopolymer impurity in the final product. These reaction conditions

therefore require careful choice of the initiator concentration and, where appropriate, the rate of the initiator feed.

It is also desirable to choose other components of the polymerization medium (for example, the solvents, surfactants, additives, and initiator) such that they have a low transfer constant towards the propagating radical. Chain transfer to these species will lead to the formation of chains which do not contain the active group.

As a general guide in choosing conditions for the synthesis of narrow polydispersity polymers, the concentration of initiator(s) and other reaction conditions (solvent(s) if any, reaction temperature, reaction pressure, surfactants if any, other additives) should be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least twice that formed in its presence. In polymerizations where termination is solely by disproportionation, this equates to choosing an initiator concentration such that the total moles of initiating radicals formed during the polymerization is less than 0.5 times that of the total moles of CTA. More preferably, conditions should be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least 5-fold that formed in its presence ($[\text{initiating radicals}]/[\text{CTA}] < 0.2$).

Thus, the polydispersity can be controlled by varying the number of moles of CTA to the number of moles initiating radicals. Lower polydispersities are obtained by increasing this ratio; higher polydispersities are obtained by decreasing this ratio.

With these provisos, the polymerization process according to the present invention is performed under the conditions typical of conventional free-radical polymerization. Polymerization employing the above described CTAs is suitably carried out with temperatures during the reaction in the range -20 to 200°C, preferably in the range 40-160°C.

The process of this invention can be carried out in emulsion, solution or suspension in either a batch, semi-batch, continuous, or feed mode. Otherwise-conventional procedures can be used to produce narrow polydispersity polymers. For lowest polydispersity polymers, the CTA is added before polymerization is commenced. For example, when carried out in batch mode in solution, the reactor is typically charged with CTA and monomer or medium plus monomer. To the mixture is then added the desired amount of initiator and the mixture is heated for a time which is dictated by the desired conversion and molecular weight. Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the CTA over the course of the polymerization process.

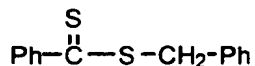
In the case of emulsion or suspension polymerization the medium will often be predominantly water and the conventional stabilizers, dispersants and other additives can be present. For solution polymerization, the reaction medium can be chosen from a wide range of media to suit the monomer(s) being used.

5 As has already been stated, the use of feed polymerization conditions allows the use of CTAs with lower transfer constants and allows the synthesis of block polymers that are not readily achieved using batch polymerization processes. If the polymerization is carried out as a feed system the reaction can be carried out as follows. The reactor is charged with the chosen medium, the CTA
10 and optionally a portion of the monomer(s). Into a separate vessel is placed the remaining monomer(s). Initiator is dissolved or suspended in reaction medium in another separate vessel. The medium in the reactor is heated and stirred while the monomer + medium and initiator + medium are introduced, for example by a syringe pump or other pumping device. The rate and duration of feed is
15 determined largely by the quantity of solution, the desired monomer/CTA/initiator ratio and the rate of the polymerization. When the feed is complete, heating can be continued for an additional period.

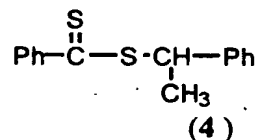
Following completion of the polymerization, the polymer can be isolated by stripping off the medium and unreacted monomer(s) or by precipitation with a
20 non-solvent. Alternatively, the polymer solution/emulsion can be used as such, if appropriate to its application.

The invention has wide applicability in the field of free radical polymerization and can be used to produce polymers and compositions for coatings, including clear coats and base coat finishes or paints for automobiles and
25 other vehicles or maintenance finishes for a wide variety of substrates. Such coatings can further include pigments, durability agents, corrosion and oxidation inhibitors, rheology control agents, metallic flakes and other additives. Block and star, and branched polymers can be used as compatibilisers, thermoplastic elastomers, dispersing agents or rheology control agents. Additional applications
30 for polymers of the invention are in the fields of imaging, electronics(e.g., photoresists), engineering plastics, adhesives, sealants, and polymers in general.

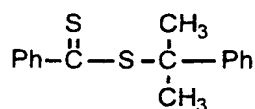
Preferred chain transfer agents applicable in the process of this invention are as follows:



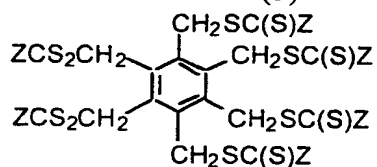
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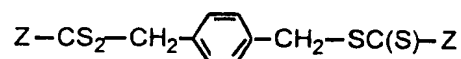
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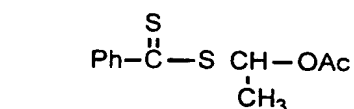
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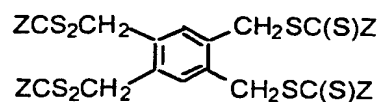
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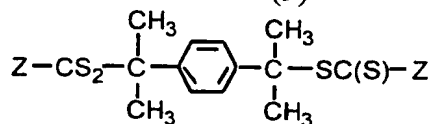
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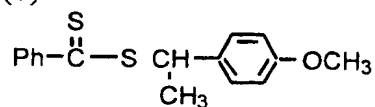
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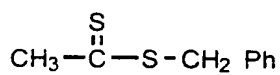
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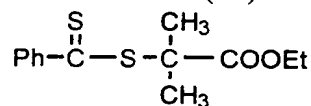
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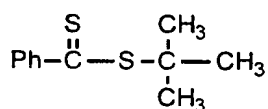
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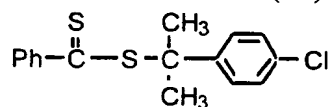
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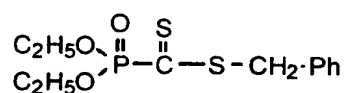
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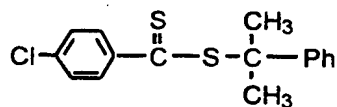
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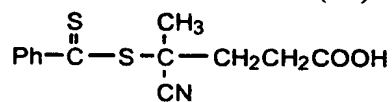
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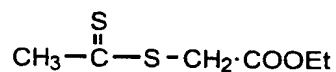
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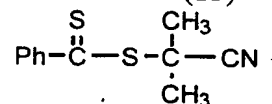
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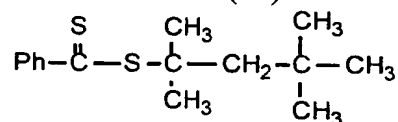
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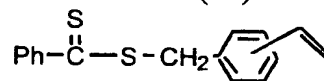
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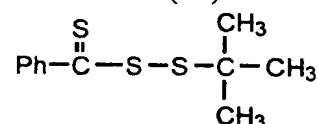
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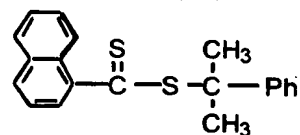
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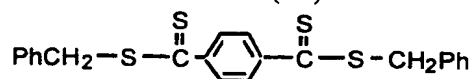
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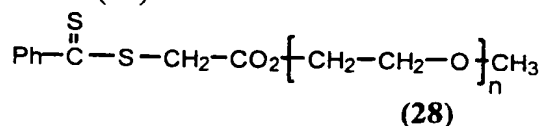
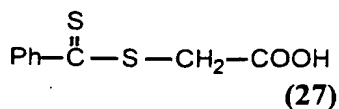
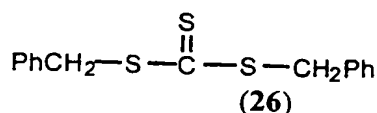
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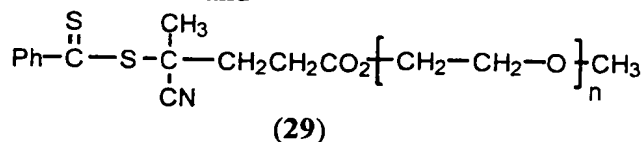
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(25)



and



wherein Z is phenyl.

EXAMPLES 1 TO 18

PREPARATION OF THIOCARBONYLTHIO COMPOUNDS

The processes for making compounds (3) to (29) are as follows: Procedures 1-11 describe the preparation of known CTA compounds. Examples 1-18 describe the synthesis of novel CTA compounds.

Procedure 1

Preparation of Dithiobenzoic acid and 4-chlorodithiobenzoic acid

Dithiobenzoic acid and 4-chlorodithiobenzoic acid were prepared according to known procedures. For instance, see the method described in German Patent 1,274,121 (1968); (CA70: 3573v).

Procedure 2

Preparation of benzyl dithiobenzoate (3) (C, p=1, R = CH₂Ph, Z = Ph)

This title compound was prepared by a modification of the one-pot procedure described in *Recueil*, 92, 601 (1973). Phenyl magnesium bromide was prepared from bromobenzene (62.8 g) and magnesium turnings (10 g) in dry tetrahydrofuran (300 mL). The solution was warmed to 40 °C and carbon disulfide (30.44 g) was added over 15 minutes whilst maintaining the reaction temperature at 40°C. To the resultant dark brown mixture was added benzyl bromide (76.95 g) over 15 minutes. The reaction temperature was raised to 50 °C and maintained at that temperature for a further 45 minutes. Ice water (1.5L) was added and the organic products extracted with diethyl ether (total 2L). The ethereal phase was washed with water (1L), brine (500 mL) and dried over anhydrous magnesium sulfate. After removal of solvent and vacuum distillation of the residue, benzyl dithiobenzoate (3) was obtained as a red oil (60.2 g, 61.7% yield), b.p. 152 °C (0.02 mmHg) [lit (Beilstein, E III 9, 1998): b.p. 179-180°C at 3 mmHg]. ¹H-nmr (CDCl₃) δ (ppm): 4.60 (s, 2H); 7.30-7.60 (m, 8H) and 8.02 (m, 2H).

Procedure 3

Preparation of 1-phenylethyl dithiobenzoate (4) (C, p=1, R = CH(CH₃)Ph, Z = Ph)

- 5 Dithiobenzoic acid (9.9 g), styrene (10 mL) and carbon tetrachloride (30 mL) were combined and the mixture heated at 70 °C for 4 hours. The resultant mixture was reduced to a crude oil. The yield of 1-phenylethyl dithiobenzoate (4) was 43.4% after purification by column chromatography (aluminium oxide (activity III), petroleum spirit 40-60 °C eluent). ¹H-nmr (CDCl₃) δ (ppm): 1.92 (d, 3H); 5.39 (q, 1H); 7.34-7.62 (m, 8H) and 8.08 (m, 2H).
- 10

Example 1

Preparation of 2-phenylprop-2-yl dithiobenzoate (5) (C, p=1, R = C(CH₃)₂Ph, Z = Ph)

- 15 A mixture of dithiobenzoic acid (10.59 g), a-methylstyrene (10 g) and carbon tetrachloride (40 mL) was heated at 70 °C for 4 hours. The resultant mixture was reduced to a crude oil which was purified by column chromatography (aluminium oxide (activity III), *n*-hexane eluent) to give 2-phenylprop-2-yl dithiobenzoate (5) (6.1 g, 32.6% yield) as a dark purple oil. ¹H-nmr (CDCl₃) δ (ppm): 2.03 (s, 6H); 7.20-7.60 (m, 8H) and 7.86 (m, 2H).
- 20

Example 2

Preparation of 1-acetoxyethyl dithiobenzoate (6) (C, p=1, R = CH(CH₃)OAc; Z = Ph)

- 25 A mixture of dithiobenzoic acid (4 g), vinyl acetate (10 mL) and carbon tetrachloride (15 mL) was heated at 70 °C for 16 hours. The resultant mixture was reduced and the residue purified by column chromatography (aluminium oxide column (activity III), *n*-hexane eluent) to give 1-acetoxyethyl dithiobenzoate (6) (3.21 g, 51.5% yield) as a dark red oil. ¹H-nmr (CDCl₃) δ (ppm): 1.80 (d, 3H); 2.09 (s, 3H); 6.75 (q, 1H); 7.34-7.60 (m, 3H) and 7.97 (m, 2H).
- 30

Example 3

Preparation of hexakis(thiobenzoylthiomethyl)benzene (9, Z=Ph) (C, p=6, R= C₆(CH₂)₆, Z = Ph)

- 35 Hexakis(thiobenzoylthiomethyl)benzene was prepared from hexakis(bromomethyl)benzene according to the method described for the preparation of benzyl dithiobenzoate (3) with the modification that the reaction mixture was heated at 50°C for 3 hours. After the usual work-up, recrystallization

5 *5^{ul}*
C6
from α -chloroform/ethanol gave the title compound as a red solid (77% yield),
m.p. 222-224 °C (dec). $^1\text{H-nmr}$ (CDCl_3) δ (ppm): 4.66 (s, 12H); 7.30-7.60 (m,
18H) and 7.94 (m, 12H).

5

Example 4

Preparation of 1,4-bis(thiobenzoylthiomethyl)benzene (8, Z=Ph) (C, p=2, R=
 $\text{C}_6\text{H}_4(\text{CH}_2)_2$, Z = Ph)

1,4-Bis(thiobenzoylthiomethyl)benzene was prepared from α,α' -dibromo-p-
xylene according to the method described for the preparation of benzyl
10 dithiobenzoate (3) with the modification that the reaction mixture was heated at
40°C for 1.5 hours. After the usual work-up, recrystallization from ethanol gave
the title compound as a red solid (66.7% yield), m.p. 95-97°C. $^1\text{H-nmr}$ (CDCl_3)
 δ (ppm): 4.60 (s, 4H); 7.34-7.60 (m, 6H) and 8.00 (m, 4H).

15

Example 5

Preparation of 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (C, p=4, R=
 $\text{C}_6\text{H}_2(\text{CH}_2)_4$, Z = Ph)

1,2,4,5-Tetrakis(thiobenzoylthiomethyl)benzene was prepared from
1,2,4,5-tetrakis-(bromomethyl)benzene according to the method described for the
20 preparation of benzyl dithiobenzoate (3) with the modification that the reaction
mixture was heated at 40 °C for 1 hour. The usual work-up gave a red solid
which was recrystallized from 1:4 benzene/ethanol to give 1,2,4,5-
tetrakis(thiobenzoylthiomethyl)benzene (47% yield), m.p. 142-143.5 °C (dec).
 $^1\text{H-nmr}$ (CDCl_3) δ (ppm): 4.65 (s, 8H); 7.30-7.58 (m, 14H) and 7.97 (m, 8H).

25

Example 6

Preparation of 1,4-bis-(2-(thiobenzoylthio)prop-2-yl)benzene (10) (C, p=2, R=
 $1,4\text{-C}_6\text{H}_4(\text{C}(\text{CH}_3)_2)_2$, Z = Ph)

1,4-diisopropenylbenzene (3.96 g) was added to a solution of
30 dithiobenzoic acid (8 g) in carbon tetrachloride (50 mL) and the mixture heated at
70 °C for 16 hours. Removal of the solvent, followed by trituration with 1:2
diethyl ether/*n*-hexane allowed isolation of the title compound as a purple solid
(2.87 g, 24.6% yield), m.p. 143-145 °C (dec). $^1\text{H-nmr}$ (CDCl_3) δ (ppm): 2.00 (s,
12H); 7.33 (m, 4H); 7.49 (m, 2H); 7.50 (s, 4H) and 7.86 (m, 4H).

Example 7

Preparation of 1-(4-methoxyphenyl)ethyl dithiobenzoate (11) (C, p=1, R=4-CH₃OC₆H₄(CH₃)CH; Z = Ph)

5 A mixture of dithiobenzoic acid (3.6 g), 4-vinylanisole (2.9 g) and carbon tetrachloride (20 mL) were heated at 70 °C overnight. The solvent was evaporated and the residue subjected to column chromatography (aluminium oxide (activity III) column, 2% diethyl ether in *n*-hexane eluent) which gave the title compound (53% yield). ¹H-nmr (CDCl₃) δ (ppm): 1.80 (d, 3H, SCHCH₃); 3.80 (s, 3H, OCH₃); 5.22 (q, 1H, SCHCH₃) and 6.88-7.97 (m, 9H, ArH).

Procedure 4

Preparation of benzyl dithioacetate (12) (C, p=1, R = CH₂Ph; Z = CH₃)

Methyl magnesium chloride (10 mL, 3M solution in THF) was diluted with THF (10 mL) and the resulting solution warmed to 40 °C. Carbon disulfide (2.28 g, 0.03 mol) was added over 10 minutes while maintaining the reaction temperature at 40 °C. The reaction was cooled to room temperature before adding benzyl bromide (5.1 g, 0.03 mol) over 15 minutes. The reaction temperature was increased to 50 °C and maintained for a further 45 minutes. Water (100 mL) was added and the organic products extracted with *n*-hexane (3 X 60 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and column chromatography (Kieselgel-60, 70-230 mesh, 5% diethyl ether in *n*-hexane eluent), pure benzyl dithioacetate was obtained as a golden oil (3 g, 55% yield). ¹H-nmr (CDCl₃) δ(ppm): 2.90 (s, 3H); 4.46 (s, 2H) and 7.31 (m, 5H).

Procedure 5

Preparation of ethoxycarbonylmethyl dithioacetate (13) (C, p=1, R = CH₂COOEt; Z = CH₃)

Methyl magnesium chloride (10 mL, 3M solution in THF) was diluted with THF (10 mL) and the resulting solution warmed to 40 °C. Carbon disulfide (2.28 g, 0.03 mol) was added over 10 minutes while maintaining the reaction temperature at 40 °C. The reaction was cooled to room temperature before adding ethyl bromoacetate (5.01 g, 0.03 mol) over 15 minutes. The reaction temperature was increased to 50 °C and maintained for a further 4 hours. Water (100 mL) was added and the organic products were extracted with ethyl acetate (3 X 60 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and column chromatography (Kieselgel-60, 70-230 mesh, 10% diethyl ether in *n*-hexane eluent), pure ethoxycarbonylmethyl dithioacetate was obtained as a golden oil (1.3

g, 24.3 % yield). ¹H-nmr (CDCl₃) δ(ppm): 1.25 (t, 3H); 2.90 (s, 3H); 4.07 (s, 2H) and 4.20 (q, 2H).

Example 8

5 Preparation of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) (C, p=1, R = C(CH₃)₂COOEt; Z = Ph)

Phenyl magnesium bromide was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium turnings (1 g) in dry THF (30 mL). The solution was warmed to 40°C and carbon disulfide (3.05 g, 0.04 mol) was added over 15 minutes while maintaining the reaction temperature at 40°C. To the resultant dark brown solution was added ethyl α-bromoisobutyrate (7 g, 0.036 mol). The reaction temperature was raised to 80°C and maintained for 60 hours. Ice water (50 mL) was added and the organic products were extracted with diethyl ether (3 X 50 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and purification by column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane/diethyl ether (9:1) eluent), 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate was obtained as a red oil (4.52 g, 42.2% yield). ¹H-nmr (CDCl₃) δ (ppm): 1.25 (t, 3H, CH₂CH₃), 1.77 (s, 6H, 2xCH₃), 4.17 (q, 2H, OCH₂CH₃), 7.35 (dd, 2H, meta-ArH), 7.52 (dd, 1H, para-ArH) and 7.95 (d, 2H, ortho-ArH).

Example 9

Preparation of 2-cyanoprop-2-yl dithiobenzoate (15) (C, p=1, R = C(CH₃)₂CN; Z = Ph)

2-Bromo-2-cyanopropane was prepared by the procedure of Chraszczewska and Popiel (*Roczniki Chem.*, 7, 74-8 (1927); *Chem. Abstr.*, (1928) 22:13436). 2-Cyanoprop-2-yl dithiobenzoate (15) was prepared from 2-bromo-2-cyanopropane by a method similar to that used to prepare compound (14) with the modification that the reaction was maintained at 50°C for 24 hours. After work-up and purification (column chromatography on Kieselgel-60, 70-230 mesh, *n*-hexane/diethyl ether 9:1 eluent), 2-cyanoprop-2-yl dithiobenzoate (15) was obtained as a dark red oil (1.9 g, 43% yield). ¹H-nmr (CDCl₃) δ (ppm): 1.95 (s, 6H, 2xCH₃), 7.38 (dd, 2H, meta-ArH), 7.57 (dd, 1H, para-ArH) and 7.92 (d, 2H, ortho-ArH). ¹³C-nmr (CDCl₃) δ (ppm): 26.5, 41.7, 120.0 (CN), 126.6, 128.5, 132.9, 144.5 and 227.

Procedure 6

Preparation of *tert*-butyl dithiobenzoate (16) (C, p=1, R = C(CH₃)₃; Z = Ph)

The synthesis of *t*-butyl dithiobenzoate (16) was carried out in two steps.

i) S-*t*-butyl thiobenzoate *t*-Butyl mercapta. (6.15 g, 0.068 mol) was added dropwise to a solution of benzoyl chloride (10.5 g, 0.075 mol) in pyridine (6 g). The resulting mixture was allowed to stir for two hours at room temperature then poured onto ice-water and the mixture extracted with diethyl ether. The organic
5 extract was washed with dilute HCl, water and brine and finally dried over anhydrous sodium sulfate. After removal of solvent and vacuum distillation, S-*t*-butyl thiobenzoate was obtained (6.64 g, 50.1% yield), b.p. 86°C (0.8 mmHg). ¹H-nmr (CDCl₃) d (ppm): 1.60 (s, 9H, 3xCH₃), 7.41 (m, 2H, ArH), 7.54 (m, 1H, ArH) and 7.94 (d, 2H, ArH). ¹³C-nmr (CDCl₃) d (ppm): 29.8, 48.0, 126.8,
10 128.3, 132.7, 138.6 and 192.9.

ii) *t*-Butyl Dithiobenzoate

A mixture of S-*t*-butyl thiobenzoate (1.94 g, 0.01 mol) and Lawesson's reagent (2.43 g, 0.006 mol) in anhydrous toluene (10 mL) was refluxed for 25 hours. After cooling to room temperature, the reaction mixture was concentrated
15 and the residue subjected to column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit/diethyl ether 19:1) The title compound was obtained as an oil, 1.37g (65.5%). ¹H-nmr (CDCl₃) d (ppm): 1.69 (s, 9H, 3xCH₃), 7.36 (m, 2H, meta-ArH), 7.50 (m, 1H, para-ArH) and 7.88 (d, 2H, ortho-ArH). ¹³C-nmr (CDCl₃) d (ppm): 28.2, 52.2, 126.6, 128.1, 131.7 and 147.0. The signal
20 due to C=S (d > 220.0 ppm) was beyond the frequency range of the spectrum.

Example 10

Preparation of 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (C, p=1, R = C(CH₃)₂CH₂C(CH₃)₃; Z = Ph)

25 A mixture of dithiobenzoic acid (5 g), 2,4,4-trimethylpentene (7.3 g) and carbon tetrachloride (25 mL) was heated at 70 °C for two days. The resultant mixture was reduced to a crude oil. Purification of the residue, by column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit 40-60°C eluent) gave 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (2.74 g, 31.7% yield) as a dark
30 red oil. ¹H-nmr (CDCl₃) d (ppm): 1.08 (s, 9H, 3xCH₃), 1.77 (s, 6H, 2xCH₃), 2.20 (s, 2H, CH₂), 7.35 (dd, 2H, meta-ArH), 7.49 (dd, 1H, para-ArH) and 7.85 (d, 2H, ortho-ArH). ¹³C-nmr (CDCl₃) d (ppm): 28.3, 31.5, 32.8, 50.5, 57.7, 126.6, 128.1, 131.5 and 147.9. The signal due to C=S (d > 220.0 ppm) was beyond the frequency range of the spectrum.

Example 11

Preparation of 2-(4-chlorophenyl)prop-2-yl dithiobenzoate (18) (C, p=1, R = 4-ClC₆H₄(CH₃)₂C; Z = Ph)

- 5 Dithiobenzoic acid (6.3 g) and 4-chloro-*a*-methylstyrene (6 g) were combined and the mixture heated at 70°C overnight. The residue was subjected to column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane as eluent) which gave the title compound as a purple solid (34.2% yield) m.p. 77-78°C. ¹H-nmr (CDCl₃) δ (ppm): 1.97 (s, 6H, 2xCH₃), 7.20-7.52 (m, 7H, ArH) and 7.86 (d, 2H, ArH). ¹³C-nmr (CDCl₃) δ (ppm): 28.4, 55.7, 126.5, 128.1, 131.9, 132.4, 142.8, 146.0. The signal due to C=S (δ > 220.0 ppm) was beyond the frequency range of the spectrum.

Example 12

- 15 **Preparation of 3- & 4-vinylbenzyl dithiobenzoates (19)** (C, p=1, R = CH₂CHC₆H₄CH₂; Z = Ph)

- A mixture of 3- & 4-vinylbenzyl dithiobenzoate (19) was synthesized from a mixture of 3- & 4-(chloromethyl)styrene by a procedure similar to that used for compound (14). The reaction was maintained at 50°C for 24 hours. After work-up and column chromatography (aluminium oxide (activity II-III), *n*-hexane/diethyl ether 49:1 eluent) the mixture of 3- & 4-vinylbenzyl dithiobenzoate (19) was obtained in 42% yield as a red oil. ¹H-nmr (CDCl₃) δ (ppm): 4.60 (s, 2H, CH₂), 5.28 (d, 1H, CH₂=CH), 5.77 (d, 1H, CH₂=CH), 6.72 (dd, 1H, CH₂=CH), 7.20-7.60 (m, 7H, ArH) and 8.00 (d, 2H, ArH).

- 25 Procedure 7

Preparation of S-benzyl diethoxyphosphinyldithioformate (20) (C, p=1, R = CH₂Ph; Z = (EtO)₂P(O))

- The title compound (20) was prepared by adapting the procedure described by Grisley, *J. Org. Chem.*, **26**, 2544 (1961).
- 30 To a stirred slurry of sodium hydride (60% dispersion in mineral oil) (8 g, 0.2 mol) in tetrahydrofuran (200 mL) was added diethyl phosphite (27.5 g, 0.2 mol) dropwise under nitrogen. The mixture was stirred until hydrogen evolution ceased (about 15 minutes). The mixture was allowed to cool in an ice-water bath and carbon disulfide (76 g, 1 mol) was added over 15 minutes followed by benzyl chloride (25.2 g, 0.2 mol) in THF (100 mL) over 20 minutes. The resultant mixture was stirred at room temperature for 24 hours. Diethyl ether (200 mL) was added and the mixture washed with water (3x200 mL). The organic layer was dried (MgSO₄), filtered and evaporated *in vacuo*. After column chromatography

Sub
C8
(Kieselgel-60, 70-230 mesh, 1:4 ethyl acetate/*n*-hexane eluent), benzyl diethoxyphosphinyldithioformate (20) was obtained (11 g, 18% yield) as a red oil. ¹H-nmr (CDCl₃) δ (ppm) 1.43 (t, 6H); 4.38 (s, 2H), 4.65 (q, 4H) and 7.30-7.45 (m, 5H).

5

Procedure 8

Preparation of tert-butyl trithioperbenzoate (21) (C, p=1; R = (CH₃)₃CS; Z = Ph)

The title compound (21) was prepared according to the procedure described by Aycock and Jurch, *J. Org. Chem.*, **44**, 569-572, (1979). The residue was subjected to column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane eluent) to give the product, *tert*-butyl trithioperbenzoate (21) as a dark purple oil in 60 % yield. ¹H-nmr (CDCl₃) δ (ppm) 1.32 (s, 9H), 7.45 (m, 3H) and 8.00 (m, 2H).

10

Example 13

Preparation of 2-phenylprop-2-yl 4-chlorodithiobenzoate (22) (C, p=1, R = C(CH₃)₂Ph; Z = *p*-ClC₆H₄)

A mixture of 4-chlorodithiobenzoic acid (13 g) and *a*-methylstyrene (15 mL) were heated at 70°C for 1 hour. To the reaction mixture was added *n*-hexane (30 mL) and heating was continued at 70°C for 16 hours. The resultant mixture was reduced to a crude oil. Purification, of the oil by chromatography (aluminium oxide column (activity II-III) *n*-hexane eluent) gave the title compound (22) as a purple oil (8.5 g, 40 %). ¹H-nmr (CDCl₃) δ (ppm) 2.00 (s, 6H); 7.30 (m, 5H); 7.55 (d, 2H) and 7.83 (d, 2H).

20

25

Example 14

Preparation of 2-phenylprop-2-yl 1-dithionaphthalate (23) (C, p=1, R = C(CH₃)₂Ph; Z = 1-naphthyl)

The procedure was analogous to that used for the preparation of compound (5). The reaction of 1-(chloromethyl)naphthalene (17.6 g, 0.1 mol), sulfur (6.4 g, 0.2 mol) and sodium methoxide (25% solution in methanol, 46 mL) in methanol (50 mL) gave 1-dithionaphthoic acid (10 g, 49%). A mixture of 1-dithionaphthoic acid (10 g) and *a*-methylstyrene (10 mL) in carbon tetrachloride (20 mL) was heated at 70 °C for 16 hours. After removal of carbon tetrachloride and unreacted *a*-methylstyrene, the residue was chromatographed (Kieselgel-60, 70-230 mesh, 5% diethyl ether in *n*-hexane eluent) to yield 2-phenylprop-2-yl 1-dithionaphthalate (23) (9.2 g, 58 %) as a dark red oil. ¹H-nmr (CDCl₃) δ (ppm) 2.06 (s, 6H); 7.29-7.55 (m, 7H); 7.66 (m, 2H); 7.85 (m, 2H) and 8.00 (m, 1H).

30

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Example 15

Preparation of 4-cyanopentanoic acid dithiobenzoate (24) (C, p=1, R = C(CH₃)(CN)(CH₂)₃CO₂H; Z = Ph)

Compound (24) can be made by a procedure analogous to that used for preparation of compounds (14) and (15). m.p. 97-99°C. ¹H-nmr(CDCl₃) δ (ppm) 1.95 (s, 3H); 2.40-2.80 (m, 4H); 7.42 (m, 2H); 7.60 (m, 1H) and 7.91 (m, 2H).

Example 16

Preparation of dibenzyl tetrathioterephthalate (25) (D, m = 2, R = CH₂Ph; Z' = 1,4-phenylene)

The sodium salt of tetrathioterephthalic acid was obtained from the reaction of a, a'-dibromo-*p*-xylene (6.6 g, 25 mmol), elemental sulfur (3.2 g, 0.1 mol), and sodium methoxide (25% in methanol, 24 mL, 0.1 mol) in methanol (30 mL) at 70 °C for 5 hours. The reaction mixture was evaporated to dryness and then dissolved in acetonitrile (50 mL). This was treated with benzyl chloride (6.3 g, 50 mmol) at room temperature for 16 hours. The suspension was filtered, the solid collected and extracted with chloroform/water. The organic extract was dried and reduced to give the title compound as a red solid (2.14 g, 21%). Melting point: 111-116 °C (dec.). ¹H-nmr (CDCl₃) δ (ppm) 4.60 (s, 4H), 7.30-7.45 (m, 10H) and 7.97 (s, 4H).

Procedure 10

Preparation of dibenzyl trithiocarbonate (26) (C, p=1, R = CH₂Ph; Z = SCH₂Ph)

The title compound was prepared according to the procedure described by Leung, M-K., *et al*, *J.Chem.Research (S)*, 478-479, (1995).

Procedure 11

Preparation of carboxymethyl dithiobenzoate (27) (C, p=1, R = CH₂COOH; Z = Ph)

The title compound was prepared according to the procedure of Jensen and Pedersen, *Acta Chem. Scand.*, **15**, 1087-1096 (1961). ¹H-nmr (CDCl₃) δ (ppm) 4.24 (s, 2H), 7.43-8.00 (m, 5H) and 8.33 (s, 1H).

Example 17

Preparation of poly(ethylene oxide) with dithiobenzoate end group (28) (C, p=1, R = CH₂COO-(CH₂CH₂O)_nMe; Z = Ph)

A mixture of carboxymethyl dithiobenzoate (27) (0.5 g, 2.36 mmol), polyethylene glycol monomethyl ether (MWt. 750) (1.7 g, 2.36 mmol), anhydrous pyridine (2 mL), dicyclohexylcarbodiimide (1.46 g, 7.1 mmol) and 4-

toluenesulfonic acid (10 mg) was stirred under nitrogen at 50 °C for 16 hours. The mixture was reduced *in vacuo* and the residue partitioned between chloroform (10 mL) and saturated aqueous sodium bicarbonate (2 mL). The organic phase was dried over anhydrous sodium sulfate and reduced to a red oil (quantitative yield based on **24**). ¹H-nmr (CDCl₃) δ (ppm) 3.35 (s, 3H), 3.53 (br.t, 2H), 3.65 (s, 50H), 3.7 (br.t, 2H), 4.23 (s, 2H), 4.30 (br.t, 2H), 7.38 (t, 2H), 7.54 (t, 1H), 8.0 (d, 2H).

Example 18

Preparation of poly(ethylene oxide) with dithiobenzoate end group (29) (C, p=1, R = C(CH₃)(CN)CH₂CH₂COO-(CH₂CH₂O)_nMe ; Z = Ph)

A mixture of 4-cyano-4-(thiobenzoylthio)pentanoic acid (**24**) (0.23 g), polyethylene glycol monomethyl ether (1.8 g, MWt 750) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine in dichloromethane (5 mL) was added by a solution of dicyclohexylcarbodiimide (0.34 g) in dichloromethane (5 mL) at room temperature under nitrogen. The mixture was stirred for two hours and filtered to remove the dicyclohexylurea by-product. The filtrate was extracted with water seven times (7x10 mL), dried over anhydrous magnesium sulfate and reduced to a red waxy solid (quantitative yield based on **24**). ¹H-nmr (CDCl₃) δ (ppm) 1.92 (s, 3H), 2.60-2.72 (m, 4H), 3.35 (s, 3H), 3.53 (m, 2H), 3.63 (s, 64H), 3.65 (m, 2H), 4.26 (t, 2H), 7.40 (t, 2H), 7.57 (t, 1H) and 7.91 (d, 2H).

The following Examples 19-88 represent non-limiting examples which demonstrate the operation of the process and the products obtainable thereby.

Examples 19 to 88

General Experimental Conditions.

In all instances, monomers were purified (to remove inhibitors) and flash-distilled immediately prior to use. The experiments referred to as controls were experiments run without the CTA unless otherwise specified. For polymerizations performed in ampoules, degassing was accomplished by repeated freeze-evacuate-thaw cycles. Once degassing was complete, the ampoules were flame sealed under vacuum and completely submerged in an oil bath at the specified temperature for the specified times. The percentage conversions were calculated gravimetrically unless otherwise indicated.

The structures of polymers and block copolymers have been verified by application of appropriate chromatographic and spectroscopic methods. Gel

permeation chromatography (GPC) has been used to establish the molecular weight and molecular weight distribution (polydispersity) of the polymers. Unless otherwise specified, a Waters Associates liquid chromatograph equipped with differential refractometer and 10⁶, 10⁵, 10⁴, 10³, 500 and 100 Å Ultrastaygel columns was used. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent. The molecular weights are provided as polystyrene equivalents. The terms M_n , M_w and M_w/M_n are used to indicate the number and weight average molecular weights and the polydispersity respectively. Theoretical molecular weights [M_n (calc)] were calculated according to the following expression:

$$M_n \text{ (calc)} = [\text{monomer}]/[\text{CTA}] \times \text{conversion} \times \text{MWt of monomer}$$

For low molecular weight polymers (degree of polymerization < 50), the end group [ZC(=S)S-] can be determined by ¹H NMR spectroscopy. In cases where the end group is (Aryl)C(=S)S- or (Alkyl)C(=S)S- the end groups can be observed in polymers with degree of polymerization ²1000 by UV-Visible spectrophotometry. Gel permeation chromatography coupled with UV-Visible spectrophotometry enables a measurement of the purity of block copolymers in these cases.

Example 19

20 Preparation of low polydispersity poly(methyl methacrylate) using 2-phenylprop-2-yl dithiobenzoate (5)

A stock solution containing methyl methacrylate (15 mL), azobisisobutyronitrile (20 mg) and 2-phenylprop-2-yl dithiobenzoate (5) (60.7 mg) in benzene (5 mL) was prepared. Aliquots (4 mL) were transferred to ampoules, degassed and sealed. The ampoules were heated at 60 °C for the times indicated in the Table.

Table 1: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60°C

Entry	time/hr	M_n	M_w/M_n	% Conv.	M_n (calc)
1	2	9 800	1.27	13.5	8 410
2	4	18 000	1.19	27.3	17 000
3	8	29 800	1.15	51.5	32 100
4	16	56 200	1.12	95.0	59 200

Example 20**Preparation of low polydispersity poly(methyl acrylate) with 1-phenylethyl dithiobenzoate (4)**

5 Stock solutions (I) of azobisisobutyronitrile (6.6 mg) in benzene (50 mL) and (II) of 1-phenylethyl dithiobenzoate (4) (87.6 mg) in benzene (50 mL) were prepared. Aliquots of stock solution (I) (2 mL) and stock solution (II) (6 mL) were transferred to ampoules containing methyl acrylate (2 mL) which were degassed, sealed and heated at 60 °C for the times specified in Table 2 below.

10 **Table 2: Molecular weight and conversion data for poly(methyl acrylate) prepared with 1-phenylethyl dithiobenzoate (4) at 60°C**

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	20	13 500	1.11	26.2
2	64	28 800	1.13	52.9
3	110	32 700	1.16	63.8

Example 21**Preparation of low polydispersity poly(*n*-butyl acrylate) with 1-phenylethyl dithiobenzoate (4)**

15 A stock solution (I) of azobisisobutyronitrile (13.4 mg) in benzene (50 mL) and a stock solution (II) of 1-phenylethyl dithiobenzoate (4) (50.6 mg) in benzene (50 mL) were prepared. Aliquots of solution (I) (10 mL) and solution (II) (20 mL) were added to a reaction vessel containing *n*-butyl acrylate (20mL). The reaction mixture was degassed, sealed and heated at 60°C for 2 hours, to give
 20 poly(*n*-butyl acrylate) (2.48 g, 13.9% conversion) with M_n 33,600, M_w 37,800 and M_w/M_n 1.13.

Example 22**Preparation of low polydispersity poly(acrylic acid) using 1-phenylethyl dithiobenzoate (4)**

25 Stock solution (I) of azobisisobutyronitrile (6.64 mg) in N,N-dimethylformamide (DMF) (25 mL) and stock solution (II) of 1-phenylethyl dithiobenzoate (4) (17.7 mg) in DMF (25 mL) were prepared. Aliquots of stock solution (I) (2 mL), stock solution (II) (6 mL) and acrylic acid (2 mL) were placed in a reaction vessel. The reaction mixture was degassed, sealed and heated at
 30 60°C for 4 hours. After removal of the solvent and excess monomer, poly(acrylic acid) (0.37 g, 17.5% conversion) was obtained. A portion was methylated (tetramethylammonium hydroxide (25% in methanol) and excess methyl iodide) to give poly(methyl acrylate) of M_n 13792, M_w 16964 and M_w/M_n 1.23.

Example 23**Preparation of low polydispersity polystyrene via bulk polymerization of styrene with benzyl dithiobenzoate (3)**

- 5 A stock solution of styrene (60 mL) and azobisisobutyronitrile (16.9 mg) was prepared. Aliquots (5 mL) were removed and transferred to ampoules containing benzyl dithiobenzoate (11.4 mg). The ampoules were degassed, sealed and heated at 60°C for the periods of time indicated in the Table below. The results are listed in Table 3 below.

10 **Table 3: Molecular weight and conversion data for polystyrene prepared with benzyl dithiobenzoate at 60°C**

Entry	time /hr	M _n	M _w /M _n	% Conv.
1 (control)	1	164 000	1.83	1.61
2	1	1 500	1.36	0.68
3	2	2 260	1.27	1.49
4	4	3 630	1.24	3.46
5	8	6 020	1.21	6.92
6	12	8 900	1.16	10.60
7	16	11 780	1.16	13.66
8	20	14 380	1.13	17.16
9	30	18 500	1.12	22.43
10	50	25 200	1.17	31.82
11	100	33 400	1.13	42.32

Example 24**Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2-phenylprop-2-yl dithiobenzoate (5)**

- 15 Polystyrene was prepared under the conditions used for Example 5 with 2-phenylprop-2-yl dithiobenzoate (5) (11.4 mg per ampoule) in place of benzyl dithiobenzoate. Results are shown in Table 4 below.

Table 4: Molecular weight and conversion data for polystyrene prepared with 2-phenylprop-2-yl dithiobenzoate at 60°C

Entry	time/hr	M_n	M_w/M_n	% Conv.
1 (control)	1	285 000	1.63	1.67
2	1	833	1.12	0.49
3	4	4 510	1.09	3.74
4	20	21 500	1.14	19.45
5	50	40 000	1.17	37.49
6	100	52 000	1.18	57.33

Example 25

- 5 **Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C**

A stock solution of styrene (10 mL) and 1-phenylethyl dithiobenzoate (4) (24.8 mg) was prepared. Aliquots (2 mL) of this solution were transferred to ampoules which were degassed, sealed and heated at 100 °C for the times

- 10 indicated in Table 5 below and analyzed by GPC.

Table 5: Molecular weight and conversion data for polystyrene prepared with 1-phenylethyl dithiobenzoate (4) at 100°C

Entry	time/hr	M_n	M_w	M_w/M_n	% Conv.
1 (Control)	6	227 000	434 000	1.91	21.7
2	6	5 800	6 300	1.09	9.7
3	20	22 000	25 000	1.15	36.8
4	64	38 500	47 000	1.22	70.6
5	120	50 000	61 000	1.23	91.9

Example 26

- 15 **Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C**

Example 25 was repeated with a threefold higher concentration of 1-phenylethyl dithiobenzoate (4) (75.6 mg) in the stock solution. The results are summarized in the Table 6 below.

Table 6: Molecular weight and conversion data for polystyrene prepared with 1-phenylethyl dithiobenzoate (4) at 100°C

Entry	time/hr	M _n	M _w	M _w /M _n	% Conv.
1	6	3 440	37 30	1.08	12.3
2	20	10 000	11 000	1.08	35.0
3	64.5	22 000	24 000	1.10	65.6
4	120	27 000	31 000	1.16	87.6

5

Example 27

Preparation of low polydispersity polystyrene via thermal polymerizations of styrene using 2-phenylprop-2-yl dithiobenzoate (5) at 100°C

Example 26 was repeated with 2-phenylprop-2-yl dithiobenzoate (5) in place of 1-phenylethyl dithiobenzoate (4) (same molar concentration). The results are listed in Table 7.

10

Table 7: Molecular weight and conversion data for polystyrene prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 100°C

Entry	time/hr	M _n	M _w	M _w /M _n	% Conv.
1	2	1 520	1 690	1.12	4.3
2	6	5 680	6 140	1.08	14.3
3	20	13 800	14 900	1.08	39.9
4	64	25 000	28 100	1.12	81.0
5	119	26 000	30 000	1.14	88.0

15

Example 28

Preparation of low polydispersity polystyrene via emulsion polymerization of styrene using benzyl dithiobenzoate (3) at 80°C

A 5-neck reaction vessel fitted with a stirrer, condenser and thermocouple was charged with water (75 g) and sodium dodecyl sulfate (5 g of 10% aqueous solution). The mixture was degassed under nitrogen at 80°C for 40 minutes. A solution of 4,4'-azobis(4-cyanopentanoic acid) (0.14 g) and benzyl dithiobenzoate (3) (0.215 g) in styrene (3.7 g) was added as a single shot. Further 4,4'-azobis(4-cyanopentanoic acid) (0.209 g) in sodium dodecyl sulfate (1% aq solution) (24 g) at a rate of 0.089mL/min along with styrene (32.9 g) at a rate of 0.2mL/min were added by syringe pumps. On completion of the initiator feed, the reaction was

25

held at 80 °C for a further 90 minutes. The isolated polystyrene had M_n 53 200; M_w/M_n 1.37 at 73% conversion.

Example 29

5 **Preparation of low polydispersity polystyrene via emulsion polymerizations of styrene using benzyl dithiobenzoate (3) at 80°C**

Example 28 was repeated with a higher concentration of benzyl dithiobenzoate (3) (0.854 g).

The isolated polystyrene had M_n 3 010; M_w/M_n 1.20 at 19% conversion.

10

Example 30

Preparation of low polydispersity poly(methyl acrylate-*block*-ethyl acrylate)

A sample of poly(methyl acrylate) (0.17 g, M_n 24 070, M_w/M_n 1.07) made with 1-phenylethyl dithiobenzoate (4) (as described in Example 20) was
15 dissolved in ethyl acrylate (2 mL) and benzene (8 mL) containing azobisisobutyronitrile (0.52 mg). The vessel was degassed, sealed and heated at 60°C for 2 hours to give poly(methyl acrylate-*block*-ethyl acrylate) (0.22 g, 10.8% conversion), M_n 30 900, M_w/M_n 1.10.

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Example 31

Preparation of low polydispersity poly(*n*-butyl acrylate-*block*-acrylic acid)

A stock solution of azobisisobutyronitrile (6.64 mg) in DMF (25 mL) was prepared. In an ampoule, poly(*n*-butyl acrylate) from Example 21, (0.5 g, M_n 33569, M_w/M_n 1.13) was dissolved in DMF (5.5 mL), acrylic acid (4 mL) and
25 stock solution (0.5 mL). The mixture was degassed, sealed and heated at 60 °C for 2 hours. After removal of the solvent and unreacted monomer, poly(*n*-butyl acrylate-*block*-acrylic acid) was obtained (0.848 g, 8.3% conversion). GPC results (after methylation of the acrylic acid of the diblock): M_n 52 427; M_w 63 342; M_w/M_n 1.19.

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Example 32

Preparation of low polydispersity polystyrene using benzyl dithioacetate (12)

A stock solution of styrene (10 mL), benzyl dithioacetate (12) (17 mg) and azobisisobutyronitrile (2.8 mg) was prepared. Aliquots (2 mL) were removed and
35 transferred to ampoules. The ampoules were degassed, sealed and heated at 60°C for the periods of time indicated in Table 8 below.

Table 8: Molecular weight and conversion data for polystyrene prepared with benzyl dithioacetate(12) at 60°C

Entry	time/hr	M _n	M _w	M _w /M _n	% Conv.
1	2	6 840	11 800	1.72	1.8
2	4	8 570	13 500	1.58	5.0
3	16	19 000	25 000	1.32	16.5
4	40	30 000	37 000	1.24	28.9

Example 33

5 Preparation of low polydispersity poly(*n*-butyl acrylate) using benzyl dithiobenzoate (3)

Stock solution (I) of azobisisobutyronitrile (13.4 mg) in benzene (50 mL) and stock solution (II) of benzyl dithiobenzoate (3) (9.62 mg) in benzene (10 mL) were prepared.

10 Aliquots of stock solution (I) (2 mL) and stock solution (II) (4 mL) were transferred to ampoules already containing *n*-butyl acrylate (4 mL). The ampoules were degassed, sealed and heated at 60°C for the periods of time indicated in Table 9 below.

15 Table 9: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with benzyl dithiobenzoate (3) at 60°C

Entry	time/hr	M _n	M _w /M _n	M _n (calc)	% Conv.
1	2	26 000	1.12	25 866	11.4
2	8	92 000	1.14	90 760	40.0

Example 34

20 Preparation of low polydispersity poly(N,N-dimethyl acrylamide) using benzyl dithiobenzoate(3)

A stock solution (I) of azobisisobutyronitrile (2.5 mg) and N,N-dimethylacrylamide (10 mL) in benzene (50 mL) was prepared. Stock solution (II) containing benzyl dithiobenzoate (3) (4 mg) in stock solution (I) (20 mL) was prepared. Aliquots of stock solutions (I) and (II) were transferred to ampoules (in the quantities indicated in the Table below). The ampoules were degassed, sealed and heated at 60°C for 1 hour. The molecular weight and polydispersity data are summarised in Table 10 below.

Table 10: Molecular weight and conversion data for poly(*N,N*-dimethyl acrylamide) prepared with benzyl dithiobenzoate (3) at 60°C

Entry	Solution (I) (mL)	Solution (II) (mL)	CTA (mg)	M _n	M _w /M _n	M _n (calc)	% Conv.
1	0	10	2	35 000	1.14	30 266	12.9
2	5	5	1	135 000	1.23	120 597	25.7
3	7.5	2.5	0.5	224 000	1.44	293 742	31.3
4 (control)	10	0	0	833 000	2.59	-	76.9

Example 35

- 5 **Emulsion polymerization of styrene in the presence of benzyl dithioacetate at 80°C with sodium dodecyl sulfate as surfactant and 4,4'-azobis(4-cyanopentanoic acid) as initiator**

A 5-neck reaction vessel fitted with a stirrer, condenser and thermocouple was charged with water (75 g) and sodium dodecyl sulfate (5 g of 10% aqueous solution). The mixture was degassed under nitrogen at 80°C for 40 minutes. A solution of 4,4'-azobis(4-cyanopentanoic acid) (0.14 g) and benzyl dithioacetate (0.155 g) in styrene (3.7 g) was added as a single shot. Further 4,4'-azobis(4-cyanopentanoic acid) (0.211 g) in sodium dodecyl sulfate (1% aq solution) (24 g) was added at a rate of 0.089 mL/min along with styrene (32.9 g) at a rate of 0.2mL/min.

On completion of the initiator feed, the reaction was held at 80°C for a further 90 minutes. The results of the experiment are summarized in Table 11.

Table 11: Molecular weight and conversion data for polystyrene prepared with benzyl dithioacetate in emulsion at 80°C

Entry	Reaction time /min	M _n	M _w /M _n	% Conversion ^a
1	75	21 000	1.27	97 ^a
2	120	29 000	1.26	98 ^a
3	180	35 000	1.33	>99
4	240	37 000	1.35	>99
5	270	38 000	1.34	>99
6	360	36 000	1.38	>99

^a Instantaneous conversion (conversion of monomer added up to time of sampling).

Example 36**Preparation of narrow polydispersity poly(styrene-*block*-*N,N*-dimethylacrylamide)**

5 The polystyrene (M_n 20300, M_w/M_n 1.15) used in this experiment was prepared by bulk polymerization of styrene (100 mL) at 60°C for 30.5 hours with azobisisobutyronitrile (28.17 mg) as initiator in the presence of benzyl dithiobenzoate (3) (228 mg).

10 A solution of the above polystyrene (0.2 g), *N,N*-dimethylacrylamide (2 mL), azobisisobutyronitrile (0.5 mg) and benzene (8 mL) was transferred to an ampoule. The resulting mixture was degassed, sealed and heated at 60°C for 1 hour. The volatiles were removed *in vacuo* to give poly(styrene-*block*-dimethylacrylamide) at 0.4 g, 10.4% conversion, with M_n 43 000 and M_w/M_n 1.24.

Example 37**Preparation of low polydispersity poly(4-methylstyrene-*block*-styrene)**

15 A mixture of polystyrene (0.5 g, M_n 20300, M_w/M_n 1.15, prepared as described in Example 36), 4-methylstyrene (2 mL), azobisisobutyronitrile (2.5 mg) and benzene (0.5 mL) were transferred to an ampoule. The resulting mixture
20 was degassed, sealed and heated at 60°C for 3 hours. Volatiles were removed under reduced pressure to give poly(styrene-*block*-4-methylstyrene) (0.81 g, 17.1% conversion, M_n 25 400 and M_w/M_n 1.19).

Example 38**Preparation of low polydispersity poly(methyl methacrylate-*block*-styrene)**

25 Poly(methyl methacrylate) (M_n 17408, M_w/M_n 1.20) was prepared under the conditions described for Example 19 with a reaction time of 4 h. This polymer (1.7 g) was dissolved in ethyl acetate and the solution transferred to an ampoule. The ethyl acetate was removed under reduced pressure and azobisisobutyronitrile
30 (2.82 mg) and styrene (10 mL) were added. The ampoule was degassed, sealed and heated at 60°C for 20 hours. After removal of the unreacted styrene, poly(methyl methacrylate-*block*-styrene) was obtained (3.9 g, 23.5% conversion) with M_n 35 000; M_w 44 000 ; M_w/M_n 1.24.

Example 39

Preparation of low polydispersity poly(*n*-butyl acrylate) via the solution polymerization of *n*-butyl acrylate at 90°C in the presence of 1,4-bis(thiobenzoylthiomethyl)benzene (8)

A stock solution of 1,1'-azobis(1-cyclohexanecarbonitrile) (8.03 mg) in benzene (10 mL) was prepared. Aliquots (1 mL) of the stock solution were added to ampoules containing *n*-butyl acrylate (4 mL), 1,4-bis(thiobenzoylthiomethyl)benzene (8) (12.7 mg) and benzene (5 mL). The contents of the ampoules were degassed, sealed and heated at 90°C for the times given in Table 12 below.

Table 12: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 1,4-bis(thiobenzoylthiomethyl)benzene (8) at 90°C

Entry	time/hr	M _n	M _w /M _n	M _n (calc)	% Conv.
1	1	5 090	1.21	5 079	4.4
2	5	57 000	1.32	65 571	56.8

Example 40

Preparation of low polydispersity poly(*n*-butyl acrylate) via the solution polymerization of *n*-butyl acrylate at 90°C in the presence of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10)

Stock solution (I) of 1,1'-azobis(1-cyclohexanecarbonitrile) (10.09 mg) in benzene (25 mL), and stock solution (II) of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) (175.1 mg) in benzene (25 mL) were prepared. Aliquots of stock solution (I) (2 mL) and stock solution (II) (4 mL) were added to ampoules containing *n*-butyl acrylate (4 mL). The ampoules were degassed, sealed and heated at 90°C for the times shown in Table 13 below.

Table 13: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) at 90°C

Entry	time/hr	M _n	M _w /M _n	M _n (calc)	% Conv.
1	5	937	1.13	952	1.6
2	16	28 000	1.21 ^a	27 365	46.0
3	42	41 000	1.37 ^a	43 904	73.8

a) trimodal molecular weight distribution

Example 41

Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 100°C in the presence of

5 hexakis(thiobenzoylthiomethyl)benzene (7)

A stock solution comprising of styrene (10 mL) and hexakis(thiobenzoylthiomethyl)benzene (7) (48.9 mg) was prepared. Aliquots of the stock solution (2 mL) were transferred to ampoules which were degassed, sealed and heated at 100°C for the times given in Table 14 below.

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Table 14: Molecular weight and conversion data for star polystyrene prepared with hexakis(thiobenzoylthiomethyl)benzene (7) at 100°C

Entry	time/hr	M _n	M _w	M _w /M _n	% Conv.
1	6	1 350	1 530	1.13	0.33
2	20	34 100	46 500	1.36	27.5
3	64	80 000	133 000	1.67	72.1

15

Example 42

Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 100°C in the presence of 1,2,4,5-tetrakis-(thiobenzoylthiomethyl)benzene (9)

A stock solution of styrene (10 mL) and 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (54.5 mg) was prepared. Aliquots (2 mL) of the stock solution were transferred to ampoules which were degassed, sealed and heated at 100°C for the times given in the Table below. Polymer was obtained by removal of the volatiles. The results are summarized in Table 15 below.

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Table 15: Molecular weight and conversion data for star polystyrene prepared with 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) at 100°C

Entry	time/hr	M _n	M _w	M _w /M _n	M _n (calc)	% Conv.
1	6	989	1 100	1.11	-	0.88
2	20	26 000	31 100	1.20	27 257	22.0
3	64	67 500	87 600	1.30	90 814	73.3

Example 43

Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 120°C in the presence of 1,2,4,5-tetrakis-(thiobenzoylthiomethyl)benzene (9)

- 5 A stock solution of styrene (10 mL) and 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (54.5 mg) was prepared. Aliquots (2 mL) of the stock solution were transferred to ampoules which were degassed, sealed and then heated at 120°C for the times given below. The polymer was isolated by removal of the volatiles. The results are summarized in Table 16
10 below.

Table 16: Molecular weight and conversion data for star polystyrene prepared with 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) at 120°C

Entry	time/hr	M _n	M _w	M _w /M _n	M _n (calc)	% Conv.
1	6	43 000	55 000	1.29	51416	41.5
2	20	75 000	109 000	1.44	100353	81.0
3	64	80 000	119 000	1.49	109770	88.6

15

Example 44

Preparation of low polydispersity poly(methyl methacrylate) using 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14)

- The method of Example 19 was used with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) (same molar concentrations). Results are summarized in
20 Table 17 below.

Table 17: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) at 60°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	2	30 000	1.89	22.7
2	4	35 000	1.72	37.1
3	8	40 000	1.66	67.4
4	16	53 000	1.48	>95

Example 45

Preparation of low polydispersity poly(methyl methacrylate) with 2-cyanoprop-2-yl dithiobenzoate (15)

- 5 The method of Example 19 was used with 2-cyanoprop-2-yl dithiobenzoate (15) (same molar concentrations). Results are summarized in Table 18 below.

10 **Table 18: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-cyanoprop-2-yl dithiobenzoate (15) at 60°C**

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	2	9 200	1.26	16.2
2	4	17 000	1.19	39.4
3	8	30 000	1.17	68.6
4	16	52 000	1.16	>90

Example 46

Preparation of low polydispersity poly(methyl methacrylate) using 2-(4-chlorophenyl)prop-2-yl dithiobenzoate (18)

- 15 The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-(4-chlorophenyl)prop-2-yl dithiobenzoate (18). Results are summarized in Table 19 below.

20 **Table 19: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-(4-chlorophenyl)propyl dithiobenzoate (18) at 60 °C.**

Entry	time/hr	M _n	M _w /M _n	% Conv.	M _n (calc)
1	2	8 840	1.25	15.1	9 390
2	4	16 200	1.17	31.0	19 330
3	8	30 400	1.13	63.3	39 260
4	16	52 800	1.14	>95	59 205

Example 47

- 25 **Preparation of low polydispersity poly(methyl methacrylate) with *tert*-butyl trithioperbenzoate (21)**

Sal
C9

5 The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with *tert*-butyl trithioperbenzoate (21). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (62.8% conversion; Mn 92 000; Mw/Mn 1.34).

Example 48

Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22)

10 The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 55 000; Mw/Mn 1.07).

Example 49

15 Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23)

The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23). After heating at 20 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 57500; Mw/Mn 1.10).

Example 50

25 Preparation of low polydispersity poly(methyl methacrylate) in presence of 2-phenylprop-2-yl dithiobenzoate (5) with benzoyl peroxide as initiator

A stock solution containing methyl methacrylate (20 mL), benzoyl peroxide (24.2 mg) and benzene (5 mL) was prepared. An aliquot (5 mL) of the stock solution was removed and 4mL of this was placed in an ampoule labelled as control run (entry 1). 2-phenylprop-2-yl dithiobenzoate (5) (54.5 mg) was added 30 to the remaining 20 mL of stock solution. Aliquots of this solution (4 mL) were transferred to four ampoules which were degassed, sealed and heated at 60 °C. The results are summarized in Table 20 below.

Table 20: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60 °C.

Entry	time/hr	M _n	M _w /M _n	% Conv.
1 (control)	2	453 000	1.81	11.1
2	2	6 080	1.40	6.8
3	4	10 300	1.28	14.8
4	8	20 000	1.17	33.4
5	16	41 000	1.13	77.9

- 5 The following example shows that polymerizations can be successfully carried out in both polar and nonpolar solvents.

Example 51

Preparation of low molecular weight and low polydispersity poly(methyl methacrylate) using 2-phenylprop-2-yl dithiobenzoate (5) in solvents such as benzene or 2-butanone (MEK).

Stock solutions were prepared by adding methyl methacrylate (15 mL) and azobisisobutyronitrile (100 mg) to the required solvent (5 mL). Aliquots (10 mL) of each stock solution and appropriate amount of 2-phenylprop-2-yl dithiobenzoate (5) (see Table 23) were transferred to ampoules which were degassed and heated at 60°C for specified times. Results are summarized in Table 21 below.

Table 21: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60 °C in various solvents

Dithioester (g)	Time (hr)	Solvent	M _n	M _w /M _n	% Conv.
1.00	63.58	Benzene	3 200	1.17	79.8
0.40	24	Benzene	6 600	1.21	95.0
1.00	63.58	2-butanone	2 800	1.17	61.3
0.40	24	2-butanone	6 300	1.19	90.2

Example 52
Solution polymerization of methyl methacrylate (25%) with 2-phenylprop-2-yl dithiobenzoate (5)

A series of methyl methacrylate polymerizations were carried out with 2-phenylprop-2-yl dithiobenzoate (5). The results (see Table 24) when compared

with control experiments clearly indicate that in the presence of dithioester there is some retardation (conversions are ca. 10% less for the same reaction time).

A stock solution containing methyl methacrylate (10 mL), benzene (30 mL) and azobisisobutyronitrile (40 mg) was prepared. The stock solution was divided into two 20mL portions. The first 20mL portion was used for the 'control' experiments (entries 1-4). 2-phenylprop-2-yl dithiobenzoate (**5**) (100 mg) was added to the second 20mL portion (entries 5-8). Aliquots (4 mL) of these solutions were transferred to ampoules which were degassed, sealed and heated at 60 °C for the specified period of time.

Results are summarized in Table 22 below.

Table 22: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5**) at 60 °C in benzene**

Entry	time/hr	parameter	control (no CTA)	with CTA (5)
1	2	M _n	98400	2880
		M _w /M _n	1.83	1.31
		% Conv.	20.3	10.7
2	4	M _n	88500	4570
		M _w /M _n	1.84	1.24
		% Conv.	35.3	23.5
3	16	M _n	69800	9250
		M _w /M _n	1.86	1.29
		% Conv.	82.3	71.6
4	30	M _n	58400	11720
		M _w /M _n	1.91	1.25
		% Conv.	95.0	88.7

15

Example 53

Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14**)**

A stock solution of azobisisobutyronitrile (14.08 mg) in styrene (50 mL) was prepared. Aliquots (5 mL) of the stock solution were transferred to ampoules containing 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**14**) (11.26 mg) which were degassed and sealed under vacuum. The ampoules were heated at 60°C for periods of time indicated in Table 23 below.

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Table 23: Molecular weight and conversion data for polystyrene prepared with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) at 60 °C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	2	1 630	1.13	1.90
2	4	3 500	1.12	4.02
3	20	24 200	1.15	26.35

Example 54

- 5 **Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2,4,4-trimethylpent-2-yl dithiobenzoate (17)**

Example 53 was repeated with the exception that the dithioester used was 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (same molar concentrations). The results are summarized in Table 24 below.

- 10 **Table 24: Molecular weight and conversion data for polystyrene prepared with 2,4,4-trimethylpent-2-yl dithiobenzoate (17) at 60 °C**

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	2	495	1.13	0.57
2	4	1 180	1.14	1.28
3	20	17 400	1.19	18.55

Example 55

- 15 **Preparation of low polydispersity polystyrene via thermal polymerization of styrene with S-benzyl diethoxyphosphinyldithioformate (20)**

A stock solution of styrene (10 mL) and S-benzyl diethoxyphosphinyldithioformate (20) (30.9 mg) was prepared. Aliquots (2 mL) of the stock solution were transferred to ampoules which were degassed and sealed. The first three ampoules (Table 25, entries 1-3), were heated at 100 °C and the final ampoule (Table 25, entry 4), was heated at 120 °C. Samples were removed at the time intervals indicated in the Table below and analyzed by GPC. The molecular weight increased linearly with % conversion and narrow polydispersities are maintained throughout the polymerization.

Table 25: Molecular weight and conversion data for polystyrene prepared with benzyldiethoxyphosphinyldithioformate (20) at 100 °C

Entry	Time/hr	M _n	M _w /M _n	% Conv.
1 ^a	6	15 900	1.11	12.1
2 ^a	20	46 100	1.13	38.0
3 ^a	64	79 300	1.25	77.8
4 ^b	22	73 500	1.37	88.9

- (a) Entries 1-3: The polymerizations were conducted at 100°C.
 (b) Entry 4: The polymerization was conducted at 120°C.

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Example 56

Preparation of low polydispersity polystyrene via thermal polymerization of styrene at 110 °C with 2-phenylprop-2-yl dithiobenzoate (5)

Example 27 was repeated with the exception that the reaction temperature used was 110 °C instead of 100 °C. After 16 hours at 110 °C, polystyrene (55% conversion) with M_n 14 400 and M_w/M_n 1.04 was obtained.

The following two Examples demonstrate the use of the invention to prepare polymers with functional end groups (e.g. carboxylic acid).

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Example 57

Preparation of low polydispersity polystyrene via thermal polymerization of styrene with carboxymethyl dithiobenzoate (27)

A stock solution of styrene (2 mL) and carboxymethyl dithiobenzoate (27) (24.8 mg) was prepared. Aliquots (1 mL) were transferred to two ampoules which were degassed, sealed and heated at 100 °C. The results are summarized in Table 26 below.

Table 26: Molecular weight and conversion data for polystyrene prepared with carboxymethyl dithiobenzoate (27) at 100 °C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	6	3 900	1.49	11.4
2	64	7 400	1.34	42.5

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Example 58**Preparation of low polydispersity polystyrene via thermal polymerization of styrene with 4-cyano-4-(thiobenzoylthio)pentanoic acid (24)**

A stock solution of styrene (2 mL) and 4-cyano-4-(thiobenzoylthio)pentanoic acid (24) (32.8 mg) was prepared. Aliquots (1 mL) were transferred to two ampoules which were degassed, sealed and heated at 100 °C. The ^{13}C -nmr spectrum of the isolated polymer (M_n 2,500; M_w/M_n 1.05) had a signal at δ 177.7 ppm indicating the presence of carboxy end-group at one end of the polystyrene. In addition, evidence from both ^1H -nmr and ^{13}C -nmr spectra indicate the presence of thiobenzoylthio end group. The results are summarized in Table 27 below.

Table 27: Molecular weight and conversion data for polystyrene prepared with 4-cyano-4-(thiobenzoylthio)pentanoic acid (24) at 100°C

Entry	time/hr	M_n	M_w/M_n	% Conv.
1	6	2 500	1.05	19.7
2	64	8 900	1.05	61.3

Example 59**Preparation of low polydispersity polystyrene via thermal polymerization of styrene with dibenzyl trithiocarbonate (26)**

A stock solution comprising of styrene (5 g) and dibenzyl trithiocarbonate (26) (43 mg) was prepared. Aliquots of the stock solution (2 g) were transferred to two ampoules which were degassed, sealed, and heated at 110 °C. The results are summarized in Table 28 below.

Table 28: Molecular weight and conversion data for polystyrene prepared with dibenzyl trithiocarbonate (26) at 110°C

Entry	time/hr	M_n	M_w/M_n	% Conv.
1	6	11,000	1.21	54
2	16	17,000	1.15	81

Example 60**Preparation of low polydispersity poly(n-butyl acrylate) using *tert*-butyl trithioperbenzoate (21)**

5 Stock solution (I) of azobisisobutyronitrile (13.4 mg) in benzene (50 mL) and stock solution (II) of *tert*-butyl trithioperbenzoate (21) (23.8 mg) in benzene (25 mL) were prepared.

10 Aliquots of stock solution (I) (2 mL) and stock solution (II) (4 mL) were transferred to ampoules containing n-butyl acrylate (4 mL). The ampoules were degassed, sealed and heated at 60 °C for the times indicated in the Table 29 which also shows the results of the polymer produced.

Table 29: Molecular weight and conversion data for poly(n-butyl acrylate) prepared with *tert*-butyl trithiophenylperformate (21) at 60°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	2	12 700	1.12	6.8
2	8	78 000	1.07	40.5
3	16	118 000	1.14 ^a	61.2
4	40	174 000	1.24 ^a	81.7

15 a Bimodal molecular weight distribution, with a small high molecular weight shoulder .

Example 61**Preparation of low polydispersity poly(N,N-dimethylaminoethyl methacrylate) using 2-phenylprop-2-yl dithiobenzoate (5)**

20 Stock solution (I) of azobisisobutyronitrile (20 mg) and N,N-dimethylaminoethyl methacrylate (15 mL) in benzene (5 mL) and stock solution (II) consisting of stock solution (I) (18 mL) and 2-phenylprop-2-yl dithiobenzoate (5) (61.1 mg) were prepared. The remainder of stock solution (I) (2 mL) was used for the control experiment. Aliquots of stock solution (II) (4 mL) were transferred to ampoules and degassed, sealed and heated at 60 °C for the times indicated in Table 30.

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Table 30: Molecular weight and conversion data for poly(N,N-dimethylaminoethyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1 (Control)	2	13 000	40.2 ^a	45.6
2	2	11 600	1.19	30.2
3	4	15 900	1.19	49.6
4	16	28 000	1.21	91.9

a Multimodal molecular weight distribution

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Example 62

Preparation of low polydispersity poly(vinyl benzoate) using 2-cyanoprop-2-yl dithiobenzoate (15)

Stock solution (I) was prepared by dissolving 2,2'-azobis(2-methylpropane) (10 mg) in vinyl benzoate (10 mL). Stock solution (II) was prepared by dissolving 2-cyanoprop-2-yl dithiobenzoate (15) (160 mg) in vinyl benzoate (10 mL). A mixture comprising stock solution (I) (0.14 mL), stock solution (II) (2.75 mL) and vinyl benzoate (3 g) was added to an ampoule. The ampoule was degassed, sealed and heated at 150 °C for 48 hours. The resultant viscous liquid was reduced *in vacuo* to poly(vinyl benzoate). M_n 3 490, M_w 4 500, M_w/M_n 1.29, 25% conversion.

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Example 63

Preparation of low polydispersity poly(vinyl butyrate) using 2-cyanopropyl dithiobenzoate (15)

Stock solution (I) was prepared by dissolving 2,2'-azobis(2-methylpropane) (10 mg) in vinyl butyrate (10 mL). A mixture comprising of stock solution (I) (0.14 mL), 2-cyanoprop-2-yl dithiobenzoate (15) (50 mg) and vinyl butyrate (5.9 g) was added to an ampoule. The ampoule was degassed, sealed and heated at 150 °C for 48 hours. The resultant viscous liquid was reduced *in vacuo* to poly(vinyl butyrate). M_n 1 051, M_w 1 326, M_w/M_n 1.26, 5% conversion.

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Example 64

Preparation of low polydispersity poly(*p*-styrenesulfonic acid sodium salt) using sodium salt of 4-cyano-4-(thiobenzoylthio)pentanoic acid

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A stock solution of 4,4'-azobis(4-cyanopentanoic acid) (23.4 mg) and *p*-styrenesulfonic acid sodium salt (4.99 g) in distilled water (25 mL) was prepared.

An aliquot of the stock solution (10 mL) was transferred to a conical flask containing sodium salt of 4-cyano-4-(thiobenzoylthio)pentanoic acid (50 mg). This solution was divided into two equal parts and transferred to two ampoules. A control experiment was carried out by placing an aliquot (5 mL) of the stock solution to another ampoule. The ampoules were degassed, sealed and heated at 70 °C for the periods of time indicated in Table 31 below.

Table 31: Molecular weight and conversion data for poly(*p*-styrenesulfonic acid sodium salt) prepared with 4-cyano-4-(thiobenzoylthio)pentanoic acid at 70°C in aqueous solution

Entry	time/hr	M _n ^a	M _w /M _n	%Conv. ^b
1 (control)	1	73 000	2.27	96.0
2	4	8 000	1.13	73.4
3	14.25	10 500	1.20	84.1

- 10 a GPC molecular weight in polystyrene sulfonic acid sodium salt standard equivalents. Operation conditions: columns, Waters' Ultrahydrogel 500, 250 and 120; eluent, 0.1M sodium nitrate/acetonitrile (80:20); flow rate, 0.8 mL/min.; detector, Waters 410 RI; injection size, 0.25 mg/50 mL.
- 15 b % Conversion was estimated by ¹H-nmr.

The following example illustrates narrow polydispersity cyclopolymer synthesis.

Example 65

Preparation of low polydispersity cyclopolymer of 2,4,4,6-tetrakis(ethoxycarbonyl)-1,6-heptadiene using 2-phenylprop-2-yl dithiobenzoate (5)

20 A mixture of 2,4,4,6-tetrakis(ethoxycarbonyl)-1,6-heptadiene (1.05 g), 2-phenylprop-2-yl dithiobenzoate (5) (24.5 mg), azobisisobutyronitrile (4.5 mg) and *o*-xylene (3 mL) were added to an ampoule degassed and sealed. The

25 ampoule was heated at 60 °C for 64 hours. After removal of all the volatiles, the cyclopolymer was isolated (0.70 g, 66.7% conversion) with M_n 6540, M_w 8920, and polydispersity 1.36. In the absence of dithiobenzoate (5), the corresponding cyclopolymer was isolated (88% conversion) with M_n 23 400, M_w 47 200, and M_w/M_n 2.01.

The following two examples demonstrate the preparation of copolymers.

Example 66

Preparation of low polydispersity poly(methyl methacrylate-*co*-styrene) in the presence of 2-phenylprop-2-yl dithiobenzoate (5)

A series of copolymerizations of styrene/methyl methacrylate (52:48 mole ratio) in the presence of 2-phenylprop-2-yl dithiobenzoate (5) was carried out. The experimental conditions were similar to those described by O'Driscoll and Huang [*Eur. Polym. J.*, **25**(7/8), 629, (1989); *ibid*, **26**(6), 643, (1990)].

Aliquots (5 mL) of styrene/methyl methacrylate (52:48 mole ratio) were transferred to eight ampoules containing dimethyl 2,2'-azobisisobutyrate (11.5 mg) four of which contained phenylprop-2-yl dithiobenzoate (5) (76.4 mg). The ampoules were degassed, sealed and placed in a constant temperature bath at 60 °C. After the specified time (see Table), the polymerizations were quenched by cooling the ampoule in cold water and the polymer was isolated by removal of all the volatiles. Results are summarized in Table 32 below.

Table 32: Molecular weight and conversion data for poly(methyl methacrylate-*co*-styrene) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60°C

Entry	time/hr	parameter	control (no CTA)	with CTA (5)
1	5	M _n	123 200	10 100
		M _w /M _n	1.67	1.21
		% Conv.	16.8	9.9
2	10	M _n	125 900	20 200
		M _w /M _n	1.75	1.17
		% Conv.	32.2	22.8
3	15	M _n	148 800	26 900
		M _w /M _n	1.82	1.22
		% Conv.	46.9	34.2
4	20	M _n	257 000	33 800
		M _w /M _n	2.39	1.21
		% Conv.	91.2	43.1

Example 67**Preparation of low polydispersity poly(acrylonitrile-co-styrene) in the presence of 2-phenylprop-2-yl dithiobenzoate (5)**

A stock solution consisting of styrene (7.27 g) and acrylonitrile (2.27 g) was prepared. An aliquot (2 g) of the stock solution was reserved for the control experiment and 2-phenylprop-2-yl dithiobenzoate (5) (28.5 mg) was added to the remaining stock solution. Aliquots of this solution (2 g) were transferred to ampoules which were degassed, sealed and heated at 100°C for the times indicated in Table 33 below.

Table 33: Molecular weight and conversion data for poly(acrylonitrile-co-styrene) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 100°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1 (control)	18	424 000	1.70	96.0
2	4	20 100	1.04	26.0
3	8	33 000	1.05	42.0
4	18	51 400	1.07	70.7

The following example illustrates synthesis of a quaternary copolymer.

Example 68**Preparation of low polydispersity quaternary copolymers of MMA/iBMA/HEMA/Styrene in the presence of 2-phenylprop-2-yl dithiobenzoate**

A stock solution was prepared comprising methyl methacrylate (1.5 g), isobutyl methacrylate (3.38 g), hydroxyethyl methacrylate (1.5 g), styrene (1.13 g), 2-butanone (2 g), azobisisobutyronitrile (0.05 g) and 2-phenylprop-2-yl dithiobenzoate (5) (0.163 g). Aliquots (4.5 g) of the stock solution were placed into ampoules which were degassed, sealed and heated at 60°C for 1 and 24 hours. The quaternary copolymer was isolated by evaporation and characterized by GPC analysis. Results are summarized in Table 34 below.

Table 34: Molecular weight and conversion data for p ly(hydroxethyl methacrylate-co-isobutyl methacrylate-co-methyl methacrylate-co-styrene) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60°C

Entry	time/hr	M _n	M _w /M _n	% Conversion
1	1	633	1.23	-
2	24	11 300	1.47	>99

5

Example 69

Preparation of low polydispersity styrene-butadiene polymers using 1-phenylethyl dithiobenzoate (4)

10 This example was carried out to demonstrate that it is possible to prepare low polydispersity styrene/butadiene (SBR, 30:70) copolymers with 1-phenylethyl dithiobenzoate (4) as chain transfer agent.

A mixture of styrene (36 g), water (197.6 g), potassium rosin soap (6.26 g), sodium formaldehyde sulfoxylate (0.060 g), tri-potassium phosphate (0.293 g), sodium carbonate (0.036 g), potassium persulfate (0.366 g) and chain transfer agent (1-phenylethyl dithiobenzoate (4) (0.09 g) or *tert*-dodecyl mercaptan (0.191 g)) was placed in a 7 oz glass bottle containing crown seal with nitrile gaskets. The bottle was degassed by purging with nitrogen, and then added butadiene (84 g). The polymerization was carried out at 50 °C and after 8 hours, SBR copolymers were obtained having M_w/M_n of 1.17 when dithioester (4) was used as the chain transfer agent, and M_w/M_n 2.08 when *tert*-dodecyl mercaptan was used as chain transfer agent. Some retardation is observed with respect to the control polymerization.

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Example 70

Preparation of low polydispersity block copolymers of methyl methacrylate and methacrylic acid in the presence of 2-phenylprop-2-yl dithiobenzoate

25 To a reaction vessel, azobisisobutyronitrile (10 mg) and a poly(methyl methacrylate) sample (1 g, made with the use of 2-phenylprop-2-yl dithiobenzoate (5) (M_n 3231, M_w/M_n 1.17), see Example 51) were dissolved in N,N-dimethylformamide (4.1 mL) and added to methacrylic acid (0.8 g). The ampoule was degassed, sealed and heated at 60°C for 16 hours. After removal of solvent, poly(methyl methacrylate-*block*-methacrylic acid) was obtained (near quantitative

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con. rsion). GPC results obtained after methylation of the diblock, gave polymer of M_n 4718 and M_w/M_n 1.18.

The following two examples illustrate the synthesis of triblock copolymers from a bifunctional chain transfer agent. In the first step, a linear polymer with thiobenzoylthio groups at each end is prepared. The second step provides an ABA triblock.

Example 71

Preparation of poly(styrene-*block*-methyl methacrylate-*block*-styrene) in the presence of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10)

Step 1: Preparation of low polydispersity poly(methyl methacrylate) with a dithioester group at each end

A stock solution (I) of azobisisobutyronitrile (20.26 mg) and methyl methacrylate (15 mL) in benzene (5 mL) was prepared. An aliquot of stock solution (I) (2 mL) was transferred to an ampoule and was used as a control experiment. 1,4-Bis(2-thiobenzoylthioprop-2-yl)benzene (10) (93.64 mg) was added to the remaining stock solution (I) to form stock solution (II). Aliquots (4 mL) of the stock solution (II) were transferred into ampoules which were degassed, sealed and heated at 60°C for the times indicated. The results are summarized in Table 35 below.

Table 35: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) at 60°C

Entry	time/hr	M_n	M_w/M_n	% Conv.
1	2	5 400	1.32	9.8
2	4	12 200	1.22	23.3
3	8	23 600	1.18	49.9
4	16	45 800	1.15	98.5

*Step 2: Preparation of poly(styrene-*block*-methyl methacrylate-*block*-styrene)*
The 8 hour poly(methyl methacrylate) sample (1.55 g, M_n 23 600, M_w/M_n 1.18) was dissolved in ethyl acetate and transferred to an ampoule. The solvent was removed under reduced pressure and azobisisobutyronitrile (3.1 mg) and styrene (10 mL) were added. The resulting solution was degassed, sealed and heated at 60°C for 20 hours. After removal of all the volatiles, the title block copolymer (orange pink colour foam) was isolated (3.91 g, 26% conversion), M_n 59 300, M_w/M_n 1.76 (trimodal).

Example 72

Preparation of poly(hydroxyethyl methacrylate-*block*-methyl methacrylate-*block*-hydroxyethyl methacrylate) in the presence of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10)

Step 1: Preparation of low polydispersity poly(methyl methacrylate) with a dithioester group at each end

Stock solution (I) consisting of azobisisobutyronitrile (20 mg) and methyl methacrylate (15 mL) in benzene (5 mL) was prepared. This solution (18 mL) was transferred to an ampoule containing 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) (93.5 mg) which was then degassed, sealed and heated at 60 °C for 8 hours. The poly(methyl methacrylate) obtained (4.7 g, 33.5 % conversion) had M_n 23 000 and M_w/M_n 1.16.

*Step 2: Preparation of narrow polydispersity poly(hydroxyethyl methacrylate-*block*-methyl methacrylate-*block*-hydroxyethyl methacrylate)*

A solution of poly(methyl methacrylate) (1.74 g, M_n 23 000, M_w/M_n 1.16) in tetrahydrofuran (14 mL), hydroxyethyl methacrylate (1 mL) and azobisisobutyronitrile (10 mg) were transferred to an ampoule which was then degassed, sealed and heated at 60 °C for 4 hours. The product poly(hydroxyethyl methacrylate-*block*-methyl methacrylate-*block*-hydroxyethyl methacrylate) (40.2 % conversion) had M_n 28 500 and M_w/M_n 1.18.

The following example illustrates the synthesis of star block copolymers with a soft inner core (n-butyl acrylate) and hard outer shell (styrene).

Example 73

Preparation of star block copolymers of n-butyl acrylate and styrene using 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9)

Step 1: Star Polymers of n-Butyl Acrylate

Stock solution (I) of 2,2'-Azobis(2,4,4-trimethylpentane) (VR-110) (8 mg) in benzene (25 mL) and stock solution (II) of 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (75 mg) in benzene (10 mL) were prepared. n-Butyl acrylate (4 mL), stock solution (I) (3 mL) and stock solution (II) (3 mL) were transferred to an ampoule which was degassed, sealed and heated at 110°C for 67 hours to give star poly(n-butyl acrylate) (39.4% conversion), M_n 23 250, M_w/M_n 2.22.

Step 2: Star Block Copolymers of n-Butyl Acrylate and Styrene

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The star poly(n-butyl acrylate) (0.5 g, M_n 23248, M_w/M_n 2.22) and styrene (2 mL) were transferred into an ampoule degassed, sealed and heated at 110°C for 16 hours. After removal of all the volatiles, the star block copolymer was obtained (1.3 g, 71.4% conversion) with M_n 82 500 and M_w/M_n 2.16.

5

The following example demonstrates the synthesis of a graft copolymer based on the use of a polymer chain with pendant dithioester groups.

Example 74

10 Preparation of graft copolymers in the presence of 3- & 4-vinylbenzyl dithiobenzoates (19)

Step 1: poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate)

A solution of vinylbenzyl dithiobenzoate (19) (100 mg, mixture of meta and para isomers), azobisisobutyronitrile (15 mg), methyl methacrylate (10 mL) in 2-butanone (10 mL) was placed in an ampoule, degassed, sealed and heated at 60 °C for 6 hours to give poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate) (3.52 g, 37.6 % conversion). GPC: M_n 102 000, M_w/M_n 2.26.

¹H-nmr analysis indicates an average of 3.5 thiobenzoylthio groups per polymer chain.

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Step 2: Poly(methyl methacrylate-graft-styrene)

A degassed solution of the poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate) from *step 1* (0.5 g) and azobisisobutyronitrile (1.0 mg) in freshly distilled styrene (5.0 mL) was heated at 60 °C for 40 hours. The polymerization gave a red gel which was insoluble in THF, acetone and chloroform. The finding that polystyrene homopolymer could not be extracted from the mixture indicates the success of the grafting experiment.

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Example 75

30 Preparation of low polydispersity poly(methyl methacrylate) by emulsion polymerization at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)

A 5-necked reaction vessel fitted with a condenser, thermocouple, and mechanical stirrer was charged with water (14.8 g), sodium dodecyl sulfate (3.0g of 10% aqueous solution) and 2-phenylprop-2-yl dithiobenzoate (5) (0.325 g) and the mixture degassed under nitrogen at 90°C for 50 minutes. Feeds of methyl methacrylate (37.5 mL, 0.316mL/min) and 4,4'-azobis(4-cyanopentanoic acid) (900 mg) in water (85 g, 0.312mL/min) were then commenced. After 65 min the

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concentration of the initiator feed was . lved [4,4'-azobis(4-cyanopentanoic acid) (450 mg) in water (94 g, 0.312mL/min)]. On completion of the feeds, the reaction was held at 90°C for a further 90 minutes. The reaction mixture was sampled periodically to provide samples for GPC analysis (see Table 36 below).

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Table 36: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 90°C in emulsion

Entry	MMA added (mL)	M _n	M _w	M _w /M _n	% Conv
1	20.5	3 550	4 530	1.27	14.2
2	37.5	12 000	15 800	1.32	41.4
3	final	26 000	34 900	1.33	89.8

- 10 The following three examples demonstrate the 'one-pot' synthesis of block copolymers by sequential monomer addition.

Example 76

Preparation of poly(methyl methacrylate-*block*-styrene) by emulsion

- 15 **polymerization at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)**

- A 5-necked reaction vessel fitted with a condenser, thermocouple, and mechanical stirrer was charged with water (37.5 g) and sodium dodecyl sulfate (3g of 10% aqueous solution). The mixture was degassed at 80°C under nitrogen for 20 40 minutes and a solution of 4,4'-azobis(4-cyanopentanoic acid) (71 mg) and 2-phenylprop-2-yl dithiobenzoate (5) (18.1 mg) in methyl methacrylate (1.6 g) was added as a single shot. Further 2-phenylprop-2-yl dithiobenzoate (5) (108 mg) in methyl methacrylate (2.5 g) was then added over 10 minutes. A feed of methyl methacrylate (15 g) was commenced at a rate of 0.188mL/min by syringe pump.
- 25 This was followed immediately by a feed of styrene (24 mL) at a rate of 0.2mL/min. Further initiator (31.5 mg) was added every 90 minutes during the feed periods. The reaction was held at 80°C for a further 120 minutes. The reaction mixture was sampled periodically to provide samples for GPC analysis (see Table 37 below).

Table 37: Molecular weight and conversion data for poly(methyl methacrylate) and poly(methyl methacrylate-*block*-styrene) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 80°C in emulsion

Entry	Sample	M _n	M _w	M _w /M _n	%Conv	M _n (calc)
1	+7.5 g MMA	9 350	11 430	1.22	43	9 430
2	+ 15 g MMA	25 000	38 600	1.54	85	31 022
3	+6 mL styrene	36 000	61 000	1.68	>99	46 790
4	+12 mL styrene	49 000	92 000	1.86	>99	57 171
5	+18 mL styrene	52 000	107 000	2.06	>99	67 552
6	+24 mL styrene	72 000	162 000	2.24	>99	77 553
7	Final	72 000	159 000	2.21	>99	77 553

The use of GPC equipped with both a diode array detector and a refractive index detector provides evidence of block formation and purity. Polymers with dithiobenzoate end groups have a strong absorption in the region 300-330 nm (exact position depends on solvent and substituents). Neither polystyrene nor poly(methyl methacrylate) have significant absorption at this wavelength.

Example 77

Preparation of low polydispersity diblock poly(butyl methacrylate-*block*-Styrene) via emulsion polymerisation at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)

Water (52 g) and sodium dodecyl sulfate (0.55g of 10% aqueous solution) were charged to 5-neck, 250mL reactor fitted with a stirrer, condenser and thermocouple and degassed under nitrogen at 80°C for 40 minutes. A solution of 4,4'-azobis(4-cyanopentanoic acid) (71 mg) and 2-phenylprop-2-yl dithiobenzoate (5) (17 mg) in butyl methacrylate (1.7 g) was added as a single shot. Further 2-phenylprop-2-yl dithiobenzoate (5) (71 mg) in butyl methacrylate (2.7 g) was then added over 10 minutes. Feeds of butyl methacrylate (16 g, 0.2485 mL/min) was then added by syringe pump. Further portions of 4,4'-azobis(4-cyanopentanoic acid) were added at 82 minutes (35 mg) and on completion of the monomer feed at 142 minutes (20 mg). Feeds of styrene (15 g, 0.2mL/min) and 4,4'-azobis(4-cyanopentanoic acid) in water (38.7 g, 0.472mL/min) were then commenced. On

completion of the feeds the reaction mixture was held at 80°C for a further 90 minutes. The reaction mixture was sampled periodically for GPC analysis.

Table 38: Molecular weight and conversion data for poly(butyl methacrylate) and poly(butyl methacrylate-*block*-styrene) prepared with phenylprop-2-yl dithiobenzoate (5) at 80°C in emulsion

Entry	Sample	M _n	M _w	M _w /M _n	% Conv	M _n (calc)
1	+10.9 mL BMA	26 000	39 000	1.50	54	22 585
2	+16.01 g BMA	63 000	77 000	1.22	95	57 742
3	final	65 500	81 000	1.23	>99	60 876
4	+11.4 mL Styrene	70 500	115 000	1.63	84	91 846
5	+15 g Styrene	78 000	136 000	1.74	84	98 579
6	Reaction Final	103 000	177 000	1.73	>99	105 710

Example 78

Preparation of low polydispersity poly(styrene-*block*-methyl methacrylate) by emulsion polymerization in the presence of benzyl dithioacetate (12)

Water (50 g) and sodium dodecyl sulfate (3g of 10% aqueous solution) were charged to a 5-neck reaction vessel equipped with a condenser, thermocouple, and mechanical stirrer. The mixture was heated at 80°C for 40 minutes while purging with nitrogen. A solution of 4,4'-azobis(4-cyanopentanoic acid) (87.5 mg) and benzyl dithioacetate (12) (104.2 mg) in styrene (2.3 g) was then added as a single shot. Feeds of styrene (13.6 g, 0.2mL/min) and an initiator solution (4,4'-azobis(4-cyanopentanoic acid) (531mg, 0.089mL/min) in water (100 g)) were commenced. On completion of the feeds the reaction temperature was increased to 90°C and the addition of feeds of methyl methacrylate (15 mL, 0.316mL/min) and 4,4'-azobis(4-cyanopentanoic acid) (265 mg) in water (100 g) (0.312mL/min) was commenced. After completion of the feeds the reaction was held at 90°C for a further 60 minutes. The reaction mixture was sampled periodically for GPC analysis.

Table 39: Molecular weight and conversion data for poly(styrene) and poly(methyl methacrylate-*block*-styrene) prepared with benzyl dithioacetate in emulsion

Entry	Sample	M _n	M _w	M _w /M _n	% Conv	M _n (calc)
1	+6 mL styrene	7 690	10 500	1.37	43	4 560
2	+12mL styrene	22 000	29 000	1.33	89	1 824
3	+15 mL styrene	24 000	32 000	1.35	>99	25 480
4	+7.5 mL MMA	35 000	49 000	1.41	92	36 390
5	+15 mL MMA	39 000	61 000	1.56	84	45 513
6	Final	41 000	65 000	1.57	87	47 620

- 5 The following two examples demonstrate the synthesis of narrow polydispersity polymers by solution polymerization including a monomer feed.

Example 79

- 10 **Preparation of low polydispersity poly(*n*-butyl acrylate) by the solution feed polymerization of butyl acrylate at 60°C in the presence of 1-phenylethyl dithiobenzoate (4)**

- 15 *n*-Butyl acrylate (10 g), ethyl acetate (10 g), azobisisobutyronitrile (50 mg) and 1-phenylethyl dithiobenzoate (4) were placed in a 100mL 3-neck round bottom flask equipped with a condenser, mechanical stirrer and thermocouple, and degassed with nitrogen over 40 minutes with stirring. The flask was then placed in a pre-heated water bath at 60°C. After 60 minutes a solution of *n*-butyl acrylate (10 g) in ethyl acetate (5 g) was added over 3 hours (0.088 mL/min) by syringe pump. On completion of the feed the reaction was held at 60°C for a further 120 minutes. The reaction mixture was sampled periodically for GPC analysis.

Table 40: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 1-phenylethyl dithiobenzoate (4) at 60°C in ethyl acetate

Entry	time/ min	M _n	M _w	M _w /M _n	% Conv	M _n (calc)
1	60	3 500	3 900	1.10	6.7	2 431
2	120	6 300	6 900	1.09	13.5	6 471
3	180	9 600	10 900	1.13	19.3	11 578
4	240	14 600	16 900	1.15	22.9	16 514
5	300	18 800	23 000	1.20	34.6	24 955
6	300	21 700	25 800	1.19	45.0	32 410

Example 80

- 5 **Preparation of low polydispersity poly(methyl methacrylate) by the solution feed polymerization of methyl methacrylate at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)**

Methyl methacrylate (15 mL), 2-butanone (5 mL), azobisisobutyronitrile (20 mg) and 2-phenylprop-2-yl dithiobenzoate (5) (0.53 g) were placed in a
 10 250mL multi-neck round bottom flask equipped with a condenser, mechanical stirrer and thermocouple, and degassed with nitrogen over 40 minutes with stirring. The mixture was then placed in a pre heated water bath at 80°C. A solution of azobisisobutyronitrile (26.7 mg) in methyl methacrylate (40 mL) and 2-butanone (13.3 mL) was then added over 4 hours (0.222mL/min). On
 15 completion of the feed the reaction was held at 80°C for a further 90 minutes. The reaction mixture was sampled periodically for GPC analysis.

Table 41: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60°C in 2-butanone

Entry	time/min	M _n	M _w	M _w /M _n	% Conv	M _n (calc)
1	60	1 280	1 550	1.20	12.9	1 549
2	120	1 860	2 340	1.26	12.4	2 085
3	180	2 900	3 730	1.28	23.5	5 074
4	240	4 100	5 200	1.27	32.0	8 445
5	final	5 400	6 800	1.26	29.7	7 838

The following example demonstrates the effectiveness of dithioesters in providing living characteristics in the suspension polymerization of methyl methacrylate. In order to achieve a low polydispersity the molecular weight must substantially smaller than the control molecular weight.

5

Example 81

Suspension polymerization of methyl methacrylate in the presence of 2-phenylprop-2-yl dithiobenzoate

This example illustrates a suspension polymerization with VAZO® 64 initiator and an ACRYLSOL® A1 polyacrylic acid suspension agent. The molecular weight of the product is controlled with 2-phenylprop-2-yl dithiobenzoate (5). The components employed are as follows where 2-phenylprop-2-yl dithiobenzoate (5) is used at 0.10 by weight of monomer:

10

	Parts by Weight
<u>Part 1</u>	
Deionized water	1490.39
ACRYLSOL® A1	<u>49.68</u>
Subtotal	<u>1540.07</u>
<u>Part 2</u>	
methyl methacrylate	451.13
2-phenylprop-2-yl dithiobenzoate	<u>0.45</u>
Subtotal	<u>451.58</u>
<u>Part 3</u>	
VAZO® 64	3.10
Deionized water	<u>3.10</u>
Subtotal	<u>6.20</u>
Final Total	<u>1997.85</u>

The initiator VAZO® 64 is commercially available from DuPont (Wilmington, DE) and ACRYLSOL® A is commercially available from Rohm & Haas (Philadelphia, PA).

15

Into a jacketed flask with internal baffles and a high speed stirrer is added methyl methacrylate monomer, a low molecular weight polyacrylic acid, and deionized water. The multi-bladed stirrer is engaged and increased in speed to about 800 rpm. The contents of the flask are heated to 65°C and the initiator is added. The contents are heated to 80°C and maintained at that temperature for two hours. The contents of the flask are filtered through cloth and washed with deionized water. The solid polymer is placed in an oven to dry. The reaction

20

product obtained is 451.13 parts (23.41%) solids, the remainder being deionized water solvent.

5 **Table 42: Molecular weight data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) by suspension polymerization**

Entry	2-phenylprop-2-yl dithiobenzoate (5) M _n / M _w / wt %	M _n	
1	0	82 000	3.75
2	0.10	52 000	2.01
3	0.50	26 500	2.13
4	1.00	16 200	1.31
5	0	82 800	3.70
6	0	9 300	3.76
7	1.00	14 900	1.52
8	1.00	15 500	1.30
9	2.00	9 150	1.24
10	2.00	9 490	1.30

Example 82

10 **Polymerization of *n*-butyl acrylate in the presence of high concentrations of 2-phenylprop-2-yl dithiobenzoate (5)**

A stock solution of 1,1'-azobis(1-cyclohexanecarbonitrile) (15 mg) in *n*-butyl acrylate (30 g) and 2-butanone (30 g) was prepared. Aliquots (5 mL) were placed in each of four ampoules and the required amounts of stock solution of the dithioester (20 mg) in 2-butanone (0.55 mL) were added to give the
 15 concentrations indicated in Table 43. The samples were degassed, sealed and heated at 80°C for 60 minutes. The polymer formed was isolated by evaporation and characterized by GPC.

Table 43: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 80°C in 2-butan ne

Entry	Dithioester	[CTA] x 10 ⁻³ M	M _n	M _w /M _n	Conv %
1	(5)	0.74	67 000	1.84	40.2
2	(5)	1.54	52 000	1.56	38.4
3	(5)	2.94	30 000	1.26	25.0
4	none	0	86 000	2.45	51.6

The following two examples illustrate the effect of the nature of the dithioester on the extent of retardation observed when using high concentrations of dithioester. The results demonstrate that the extent of retardation can be minimized by selecting a particular dithioester according to the monomer being polymerized on the basis of the considerations discussed in the text.

Example 83

Polymerization of Styrene with various Dithioesters.

A stock solution of 1,1'-azobis(1-cyclohexanecarbonitrile) (15 mg) in styrene (15 g) and toluene (15 g) was prepared. Aliquots (5 mL) were placed in each of four ampoules and the required amounts of a stock solution of the appropriate dithioesters were added to give the concentrations indicated in Table 44. The samples were degassed, sealed and heated at 110°C for the times indicated in Table 44. The polymer formed was isolated by evaporation and characterized by GPC.

Table 44: Molecular weight and conversion data for polystyrene prepared with various dithioesters at 110°C in toluene

Entry	CTA	time (min)	M _n	M _w /M _n	Conv %	[CTA] x 10 ⁻² M
1	2-cyanoprop-2-yl dithiobenzoate (15)	60	2 330	1.08	15.4	2.2
2	2-cyanoprop-2-yl dithiobenzoate (15)	120	4 100	1.07	27.2	2.2
3	2-phenylprop-2-yl dithiobenzoate (5)	60	2 010	1.07	1.40	1.8
4	2-phenylprop-2-yl dithiobenzoate (5)	120	3 250	1.07	16.9	1.8
5	none	60	62 000	1.57	21.3	0
6	none	120	68 000	1.62	28.2	0

Example 84

5 **Polymerizations of *n*-butyl acrylate with various Dithioesters**

A stock solution of dimethyl 2,2'-azobisisobutyrate (7.5 mg) in *n*-butyl acrylate (15 g) and 2-butanone (15 g) was prepared. Aliquots (5 mL) were placed in each of four ampoules and the required amounts of a stock solution of the dithioester were added to give the concentrations indicated in Table 45. The
 10 samples were degassed, sealed and heated at 80°C for the times indicated in Table 45. The polymer formed was isolated by evaporation and characterized by GPC.

Table 45: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with various dithioesters at 80°C in in 2-butanone

Entry	CTA	time (min)	M _n	M _w /M _n	Conv %	[CTA] x 10 ⁻² M
1	2-phenylprop-2-yl dithiobenzoate (5)	60	275	1.11	2.1	2.4
2	2-phenylprop-2-yl dithiobenzoate (5)	120	555	1.20	3.6	2.4
3	benzyl dithiobenzoate (3)	60	790	1.16	3.2	2.6
4	benzyl dithiobenzoate (3)	120	1 397	1.21	7.3	2.6
5	benzyl dithioacetate (12)	60	3 550	1.18	25.1	3.4
6	benzyl dithioacetate (12)	120	6 100	1.17	49.8	3.4
7	none	60	76 000	2.63	67.8	0
8	none	120	89 000	2.34	80.8	0

5 The following two Examples demonstrate the use of the invention in mini-emulsion polymerization.

Example 85

Preparation of low polydispersity polystyrene via mini-emulsion polymerization with benzyl dithiobenzoate (3) at 70°C

10 A 5-neck reaction vessel fitted with a stirrer, condenser and thermocouple was charged with water (75 g) and sodium dodecyl sulfate (215.2 mg), cetyl alcohol (53 mg), sodium bicarbonate (16.7 mg). The mixture was then homogenized for 10 minutes. Styrene (18.84 g) was added and the mixture homogenized for a further 5 minutes. The reaction mixture was stirred (300 rpm)
15 for 40 minutes while the temperature was raised to 70 °C. Benzyl dithiobenzoate (3) (107 mg) and 2,2'-azobis(2-cyano-2-butane) (40.7 mg) were then added. The reaction mixture was heated at 70 °C with stirring (300 rpm) for 6 hours and sampled periodically for GPC analysis.

Table 46: Molecular weight and conversion data for polystyrene prepared with benzyl dithiobenzoate (3) in mini-emulsion at 70°C

Entry	time /min	M_n	M_w/M_n	% Conversion
1	60	2 080	1.78	7
2	120	2 980	1.21	11
3	180	4 450	1.11	14
4	360	6 470	1.23	33

A control experiment (no dithioester) gave M_n 480 000, M_w/M_n 2.4, conversion 99% after 360 minutes.

Example 86

Preparation of low polydispersity polystyrene by mini-emulsion polymerization with benzyl dithiobenzoate (3) at 70°C

An experiment carried out under conditions similar to those used for Example 85 but with potassium persulfate as initiator gave polystyrene M_n 6 770, M_w/M_n 1.15, conversion 26% after 360 minutes.

Example 87

Preparation of low polydispersity poly(ethylene oxide-*block* styrene)

A mixture of styrene (2.25 g) and dithioester (28) (0.14 g) was placed in an ampoule which was then degassed, sealed and heated at 110°C for 5.5 hours. The excess styrene was evaporated to give the title block copolymer with M_n 11 700 and M_w/M_n 1.4 at 27% conversion. Examination of the product by Gel permeation chromatography coupled with UV-Visible spectrophotometry established the presence of the dithiobenzoate end group in the final block copolymer.

Example 88

Preparation of low polydispersity poly(ethylene oxide-*block* styrene)

A mixture of styrene (4.5 g) and dithioester (29) (0.5 g) was placed in an ampoule which was then degassed, sealed and heated at 110°C for 21 hours. The excess styrene was evaporated to give the title block copolymer with M_n 7 800 and M_w/M_n 1.07 at 40% conversion.